GRADIENT ANALYSIS OF CARBON MONOXIDE AND METHANE IN POLLUTED AND OTHER NEARSHORE HABITATS

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Gradient Analysis of Carbon Monoxide and Methane in Polluted and Other Nearshore Habitats

by

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ABSTRACT

A system for the determination of dissolved gases in seawater by gas chromatography was constructed and used to find the concentrations of methane and carbon monoxide in a variety of habitats around the Monterey Peninsula. Methane was shown to have a maximum of 2.8×10^{-4} ml/l at 50 meters at the open ocean station, with a surface value of 1.1×10^{-4} ml/l. The surface waters at the nearshore stations were almost three times this value. Methane was also shown to be an effective tracer for sewage effluent. The carbon monoxide maximum of 2.1×10^{-4} ml/l was found at 15 meters which correlated closely with primary productivity (Rowney 1973). The surface value of 0.81×10^{-4} ml/l was lower than the nearshore values. All stations sampled were found to be highly supersaturated with both gases. This indicates that in this area, the ocean is a major source of both methane and carbon monoxide.

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I. INTRODUCTION

The ocean has been shown to be supersaturated with carbon monoxide (Swinnerton, Linnenbom, and Lamontagne, 1970). The sources for this gas may be plants (Chapman and Tocher, 1966; Delwiche, 1970; Loewus and Delwiche, 1963), animals (Pickwell and Barham, 1964; Pickwell, 1970; Barham, 1963; Wittenberg, 1960), and microorganisms (Junge, et. al., 1971). These results led to the hypothesis that carbon monoxide production might be related to primary productivity. The highly productive waters of Monterey Bay were thought to be an excellent location to test this hypothesis.

Methane has also been reported as being present in surface waters (Swinnerton, Linnenbom, and Cheek, 1969). Since this gas is a product of anaerobic decomposition of organic matter it was felt that it might be useful as a pollution tracer from sewage outfalls. Again, Monterey Bay provides an excellent environment for these studies.

In order to measure these gases, the highly sensitive methods of gas chromatography were used. The gas chromatograph has long been one of the analytical chemist's most useful instruments. It was not until 1962 that a practical system for oceanographic analyses was developed (Swinnerton, Linnenbom, and Cheek, 1962). Today, the shipboard determination of dissolved gases by gas chromatography is one of the most valuable methods available to the chemical oceanographer.

II. EQUIPMENT

The system used was essentially that described by Swinnerton, Linnenbom, and Cheek (1968). A calibration system was added and minor modifications were made in the sample transfer system. The entire system is shown in Figure 1.

A. GAS TRAPPING SYSTEM

The separation is accomplished in four major steps. They are sample transfer, stripping, trapping, and backflushing.

1. Sample Transfer

A helium line is connected to the side port of a Swagelok heat exchanger "T". A standard taper joint is attached to the bottom of this "T" that fits into the filled sample bottle. A 1/8" stainless steel tube runs from the bottom of the sample bottle through the heat exchanger "T" and is connected to the bottom of the stripping chamber.

Transfer of the sample is accomplished by displacement with helium. The helium flow is controlled by a micrometer valve. The helium forces the water sample through the stainless steel tube into the stripping chamber. A toggle valve is located in the helium line to release the pressure in the sample bottle after transfer.

2. Stripping Chamber

The stripping chamber is a glass tube 65 mm. in diameter and 45 cm. tall. It is fitted with a coarse fritted disc at the bottom and a 10 cm. neck, 2 cm. in diameter, at the top. "Purge helium" is introduced just below the fritted disc. It is controlled by a Teflon stopcock and its flow rate is held at 70 ml/min by a Brooks flow control valve.

Just above the fritted disc is the sample inlet. It is connected

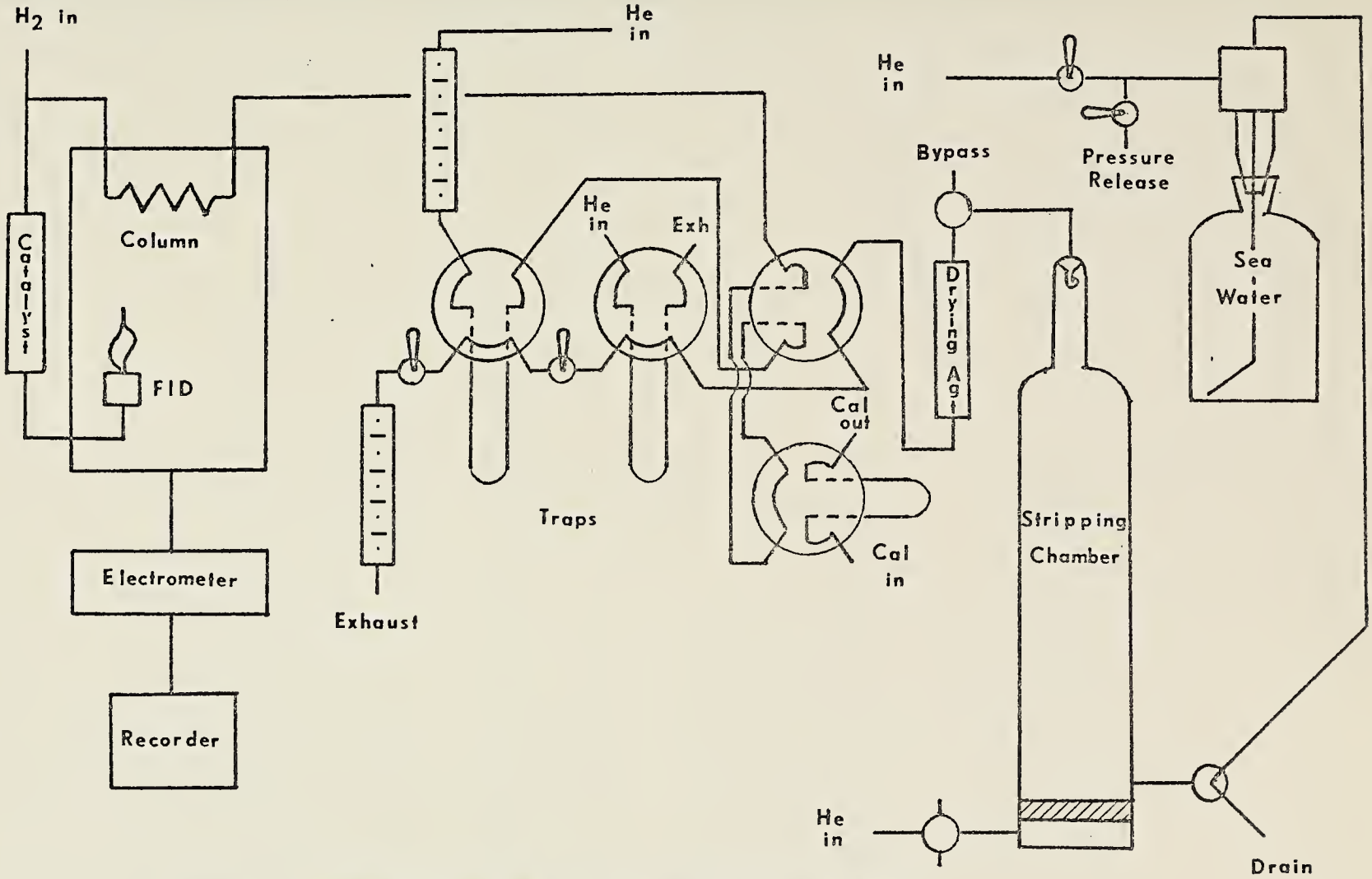

Figure 1. Schematic diagram of the dissolved gas analysis system. System is shown in the analyze position.

to one port of a Y-type stopcock. This stopcock allows the operator to purge the line prior to sample transfer, transfer the sample, and later, drain the chamber.

The neck of the chamber is fitted with a ground glass joint. This provides an opening for cleaning and a place to insert the magnetic stirring bar. At the top of the neck is a modified Kjeldahl tip. This breaks any bubbles and thus keeps water from being carried into the rest of the system.

3. Trapping Columns

The traps were constructed of 3/16" stainless steel tubing. The first trap was packed with ten inches of 60/80 mesh activated alumina and the second with a mixture containing ¼ activated charcoal and 3/4 30/60 mesh 5A molecular sieve. They were connected across the sample loop ports of Perkin-Elmer gas sampling valves (See Figure 2).

Toggle valves were placed on either side of the activated charcoal/ molecular sieve trap. These allowed the trap to be isolated while holding a sample and thus precluded any gas leakage prior to analysis.

4. Backflush Lines

A constant flow of helium had to be maintained across the column in the chromatograph. This was accomplished in that in the trap position, the carrier gas was passing through the gas sampling valve for the activated charcoal/molecular sieve trap to the chromatograph. In the analyze position, the carrier gas backflushed the trapped sample gases to the chromatograph. The flow rate was maintained at 30 ml/min by a Brooks flow control valve.

After the analysis was complete, the activated alumina trap was backflushed with line helium to remove trapped gases. Since this trap was

not analyzed, a cap was placed on the exhaust port when the valve was in the trap position, in order to conserve helium and maintain pressure for stripping. It also kept water from backing up into the system.

B. CALIBRATION SYSTEM

In order to have consistent calibrations, a gas sampling valve with a 1 ml. sample loop was incorporated into the system. This enabled a known gas mixture to be introduced into the trapping system or directly into the chromatograph. A diagram showing the calibration system is shown in Figure 2.

C. GAS CHROMATOGRAPH

A Varian Aerograph Model 600C gas chromatograph was obtained on loan from the Department of Physics and Chemistry. It was equipped with a flame ionization detector (FID), a tube-type electrometer, and a Model 328 isothermal temperature controller.

1. Modifications

The original column was replaced with a four foot, 3/16", stainless steel column packed with 30/60 mesh 5A molecular sieve. Upon conditioning (heating for two hours at 150 ^{o}C in a helium atmosphere), this column provided adequate separation of carbon monoxide and methane.

The normal carrier-gas port and injection port on the gas chromatograph were bypassed since the already mixed unknown and carrier gas were entering from the traps, i.e., there was a direct connection of the line from the activated charcoal/molecular sieve trap to the column.

The hydrogen port was also sealed since the hydrogen was introduced prior to a catalyst tube.

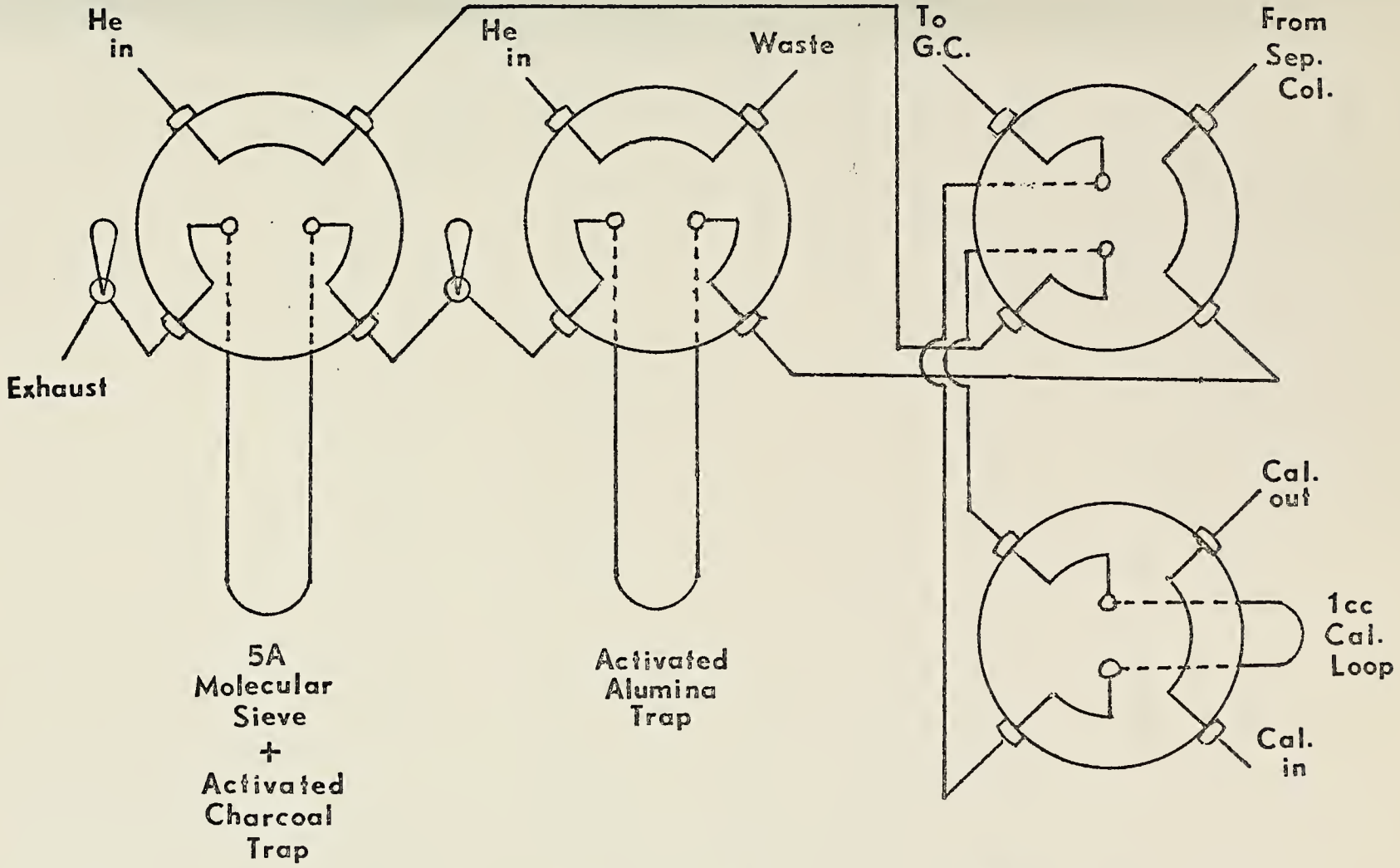

Figure 2. Detailed schematic diagram of the calibration system and traps. System is shown in the trap position with a calibration sample being injected into the chromatograph.

D. CATALYST FURNACE

The flame ionization detector is not sensitive to carbon monoxide. Therefore, the carbon monoxide must be converted to methane prior to analysis. This is accomplished by passing the carbon monoxide over a heated nickel catalyst in the presence of hydrogen (Porter and Vollman, 1962).

The catalyst furnace was placed between the analytical column and the detector. It consisted of a 10 cm., ¼", stainless steel tube in which the catalyst was placed. An aluminum block 7.5 cm. long and 2.5 cm. in diameter was placed around this tube as a heat sink. This assembly was placed flush inside a threaded quartz tube which was wound with a Nichrome wire heater. To prevent fire and provide additional insulation, the heater was placed in a Transite box which was mounted on the side of the chromatograph. The temperature was monitored with a five ohm iron-constantan thermocouple attached to the auxillary terminal of the temperature controller. Temperature control was regulated with a Variac controller.

E. RECORDER

A Varian Model G-14 strip chart recorder was used to record the output of the electrometer. It was set for 1 mv. full scale deflection and run at a chart speed of 1 in./min.

III. EXPERIMENTAL METHODS

A. SAMPLE COLLECTION

Five nearshore stations were taken in kelp beds around the Monterey Peninsula as described in Table 1 and Figure 3. The stations varied from a relatively calm area at Del Monte Beach to areas of extreme turbulence on the exposed coast at Point Pinos and Point Joe. These stations were occupied periodically from 31 October 1972 to 15 December 1972.

Sampling in the nearshore areas was done from a forty foot boat. In order to minimize contamination from the exhaust, the boat was allowed to drift to a stop in the kelp beds prior to sampling. Samples were taken in a Van Dorn type bottle that was rigged with hand lines for lowering and tripping.

Samples were collected in 500 ml. reagent bottles by filling from the bottom with a surgical rubber tube. The bottles were then sealed with a standard taper ground glass stopper. This reduced the possibility of air contamination and outgassing from the sample. If the samples were to be stored before analysis, a small amount of sodium azide (NaN_3) was added to kill any organisms that might alter the dissolved gas concentrations.

In order to have open ocean values to compare with those found in the nearshore habitats, a deep station was taken in the Monterey Canyon aboard R/V Acania (see Table 1). Samples were taken at depths of 0, 5, 15, 30, 50, 75, 100, 200, 500, 700, and 1000 meters using standard Nansen bottles. In addition, a cast was made at 0, 5, 12, 18, and 45 meters for determination of primary productivity (see Rowney, 1973).

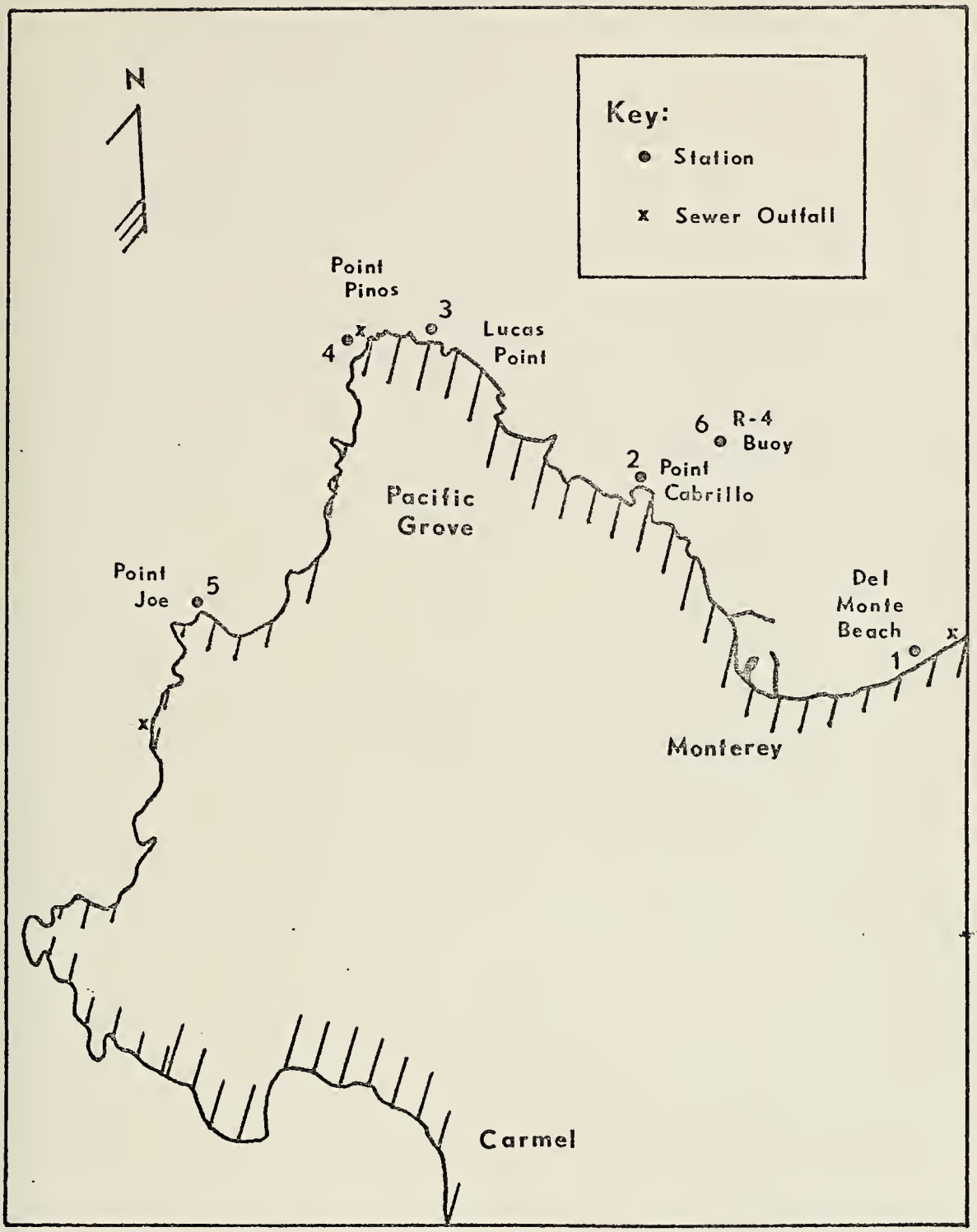

Figure 3. Chart showing location of nearshore stations.

Table 1

Seawater Sampling Stations

Station Number	Name	Positions
1	Del Monte Beach	36° 36.3' N 121° 52.4' W
2	Point Cabrillo	36° 37.4' N 121° 54.1' W
3	Point Pinos North	36° 38.3' N 121° 55.4' W
4	Point Pinos South	36° 38.3' N 121° 56.3' W
5	Point Joe	36° 36.8' N 121° 57.3' W
6	R-4 Bell Buoy	36° 37.5' N 121° 54.3' W
7	Monterey Canyon	36° 44.3' N 122° 07.2' W

Transects were taken across Del Monte Beach, from Del Monte Beach to the R-4 buoy, and from Point Cabrillo to the R-4 buoy. These were taken to determine any gradients present.

B. SAMPLE ANALYSIS[1]

The sample bottle was connected to the system by a ground glass joint. Helium was introduced above the sample forcing the water through a stainless steel tube to the drain valve. The first few milliliters were discarded to ensure flushing of the transfer line. The stripping chamber, which had been previously drained to the 500 ml. mark, was then filled to the zero mark. This method of transfer minimized contact with the atmosphere and thus reduced the chance of contamination.

"Purge helium" was introduced below the fritted disc and allowed to bubble through the sample for twelve minutes. A magnetic stirring bar in the chamber increased the residence time of the bubbles in the sample. After twelve minutes, no measurable amounts of carbon monoxide or methane were left in the sample and as prior tests showed, no leakage from the cold traps had occurred. Before reaching the traps, the gas passed through a magnesium perchlorate drying agent to remove any water vapor.

Trapping of the gases took place on two series-connected cold traps. They were both maintained at -77°C with an acetone-dry ice bath, in a Dewar flask. The first trap was an activated alumina column which removed any hydrocarbons higher than methane as well as carbon dioxide. The second, a mixture of 1/4 activated charcoal and 3/4 molecular sieve, removed carbon monoxide, methane, and air. In the twelve minute purging time, most

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[1] A complete, step-by-step, analysis check list is included in Appendix A.

of the air was bled off the trap and only a small amount of residual oxygen remained. This proved to be no problem since the analytical column in the gas chromatograph provided sufficient separation of these gases.

After the twelve minutes of purging time, isolation valves on either side of the activated charcoal/molecular sieve trap were closed. The acetone-dry ice bath was removed and replaced with one of boiling water. The trap was now backflushed into the analytical column in the gas chromatograph. The activated alumina trap was backflushed to the atmosphere since its contents were not of importance to this experiment.

Retention times for a column temperature of 48°C and a flow rate of 30 ml/min were: air, 1.5 min.; methane, 3.0 min.; carbon monoxide, 4.25 min. Analysis was complete seven minutes after injection of the sample into the gas chromatograph.

To ensure complete conversion of carbon monoxide to methane, the catalyst furnace was held between 300-320 °C. This also reduced tailing on the carbon monoxide peak.

Figure 4 shows a chromatogram from a sample analysis. The concentration of each gas is proportional to the area under its respective peak. In order for these areas to be meaningful, a method of calibration was needed.

To accomplish this, a calibration gas is used. A calibrated gas mixture of 70.3 ppm methane and 71.1 ppm carbon monoxide in air was obtained from the Naval Research Laboratory, Washington D.C. Preliminary work showed no measurable difference in the results when the gas was introduced into the traps or directly into the gas chromatograph, therefore direct injection was used to conserve time.

Figure 5 shows the results of a calibration run. Now, the response of the system to a known concentration of gas was known and the unknown

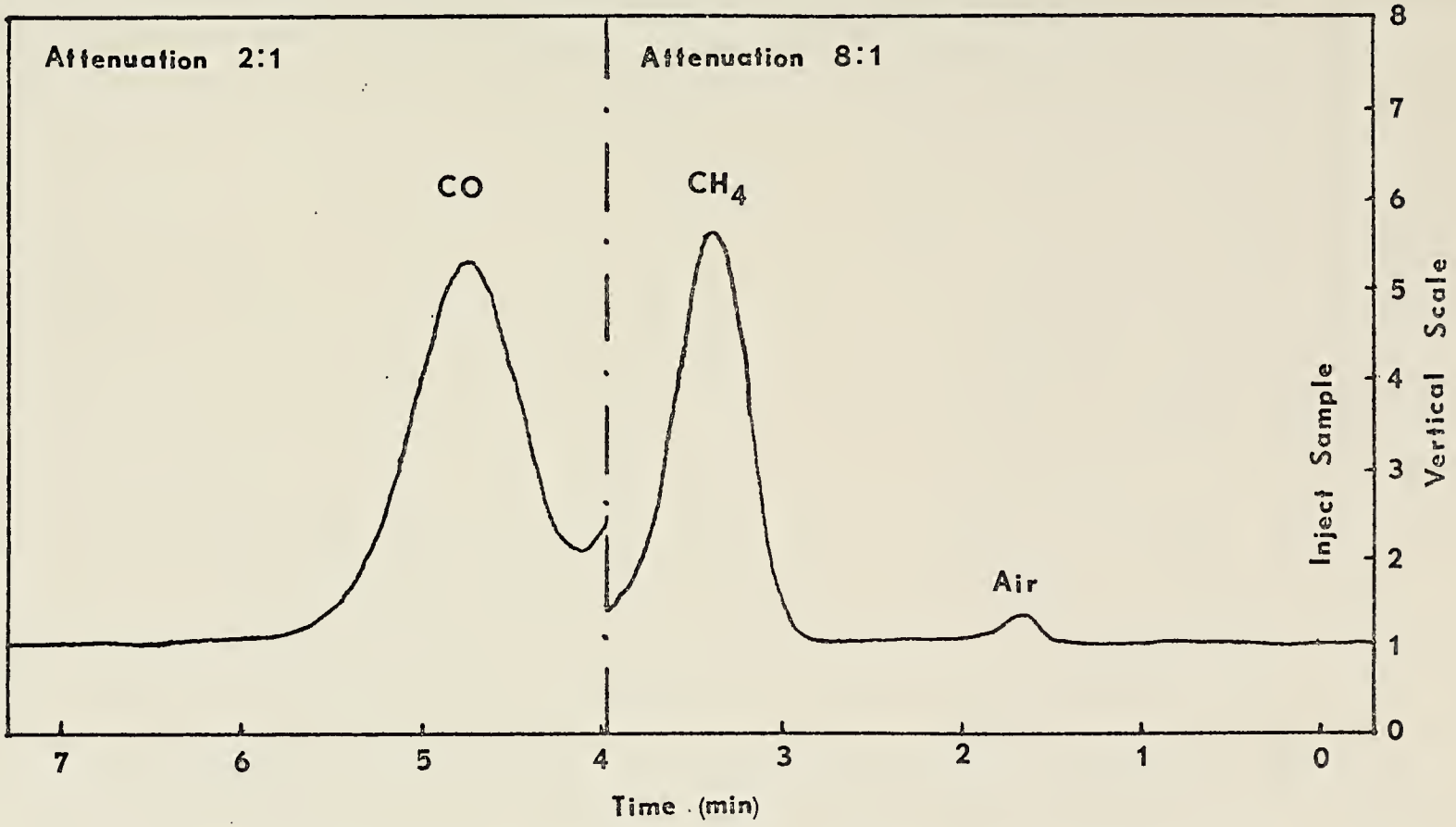

Figure 4. Chromatogram from a sample run. Signals from the electrometer have been attenuated 2:1 for CO and 8:1 for CH_4.

concentrations could be determined by comparing areas. Calibrations were run periodically along with the samples. In addition to calibrating the system, these calibration checks were also used to determine if the catalytic conversion of carbon monoxide to methane was complete.

After the sample was run, the area under each peak was determined in the following manner. The height of the peak and the width at half height were measured with a set of dial calipers. These values were multiplied together to get the raw area; a range and attenuation factor from the electrometer setting was applied to get the effective area. These calculations were carried out on the IBM 360/67 computer. A copy of the program is included in Appendix C.

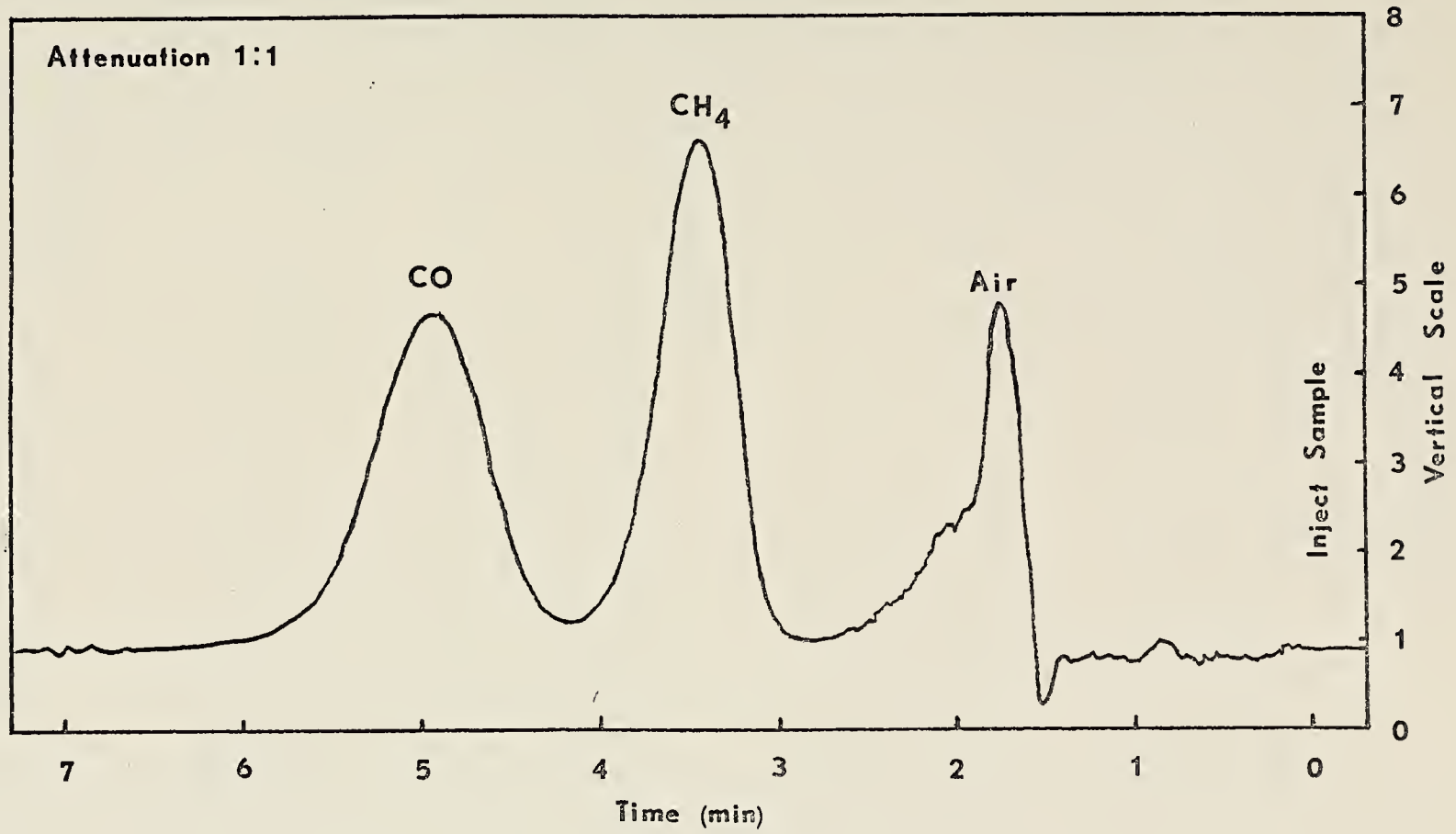

Figure 5. Chromatogram from a calibration run.

IV. RESULTS

A. OPEN OCEAN DEEP STATION

Station seven (Table 1) was located on the axis of the Monterey Submarine Canyon in 1375 meters of water. An eleven bottle cast to 1000 meters was taken. The profiles from this cast are shown in Figures 6 and 7 and tabulated in Tables 2 and 3.

1. Methane

The methane profile (Figure 6 and Table 2) shows a surface concentration of 1.1×10^{-4} ml/l. This value increases with depth to 50 meters. From 50 to 100 meters it decreases slightly and then more rapidly to 200 meters. It then decreases linearly with depth at a rate of 0.125×10^{-4} ml/l/100 m to 1000 meters.

2. Carbon Monoxide

Figure 7 and Table 3 shows a carbon monoxide concentration of 0.81×10^{-4} ml/l at the surface. This value increases sharply to almost 2×10^{-4} ml/l at 15 meters and then decreases to near surface values at 100 meters. From 100 to 1000 meters, the concentration decreases to only trace amounts.

3. Primary Productivity

Primary productivity measurements made by Rowney (1973) at the same station are shown in Figure 8. Note the relatively high values in the upper 12 meters.

B. TEMPORAL STUDIES

A temporal study of carbon monoxide and methane was conducted in each of the five nearshore habitats. The plots of concentration versus time

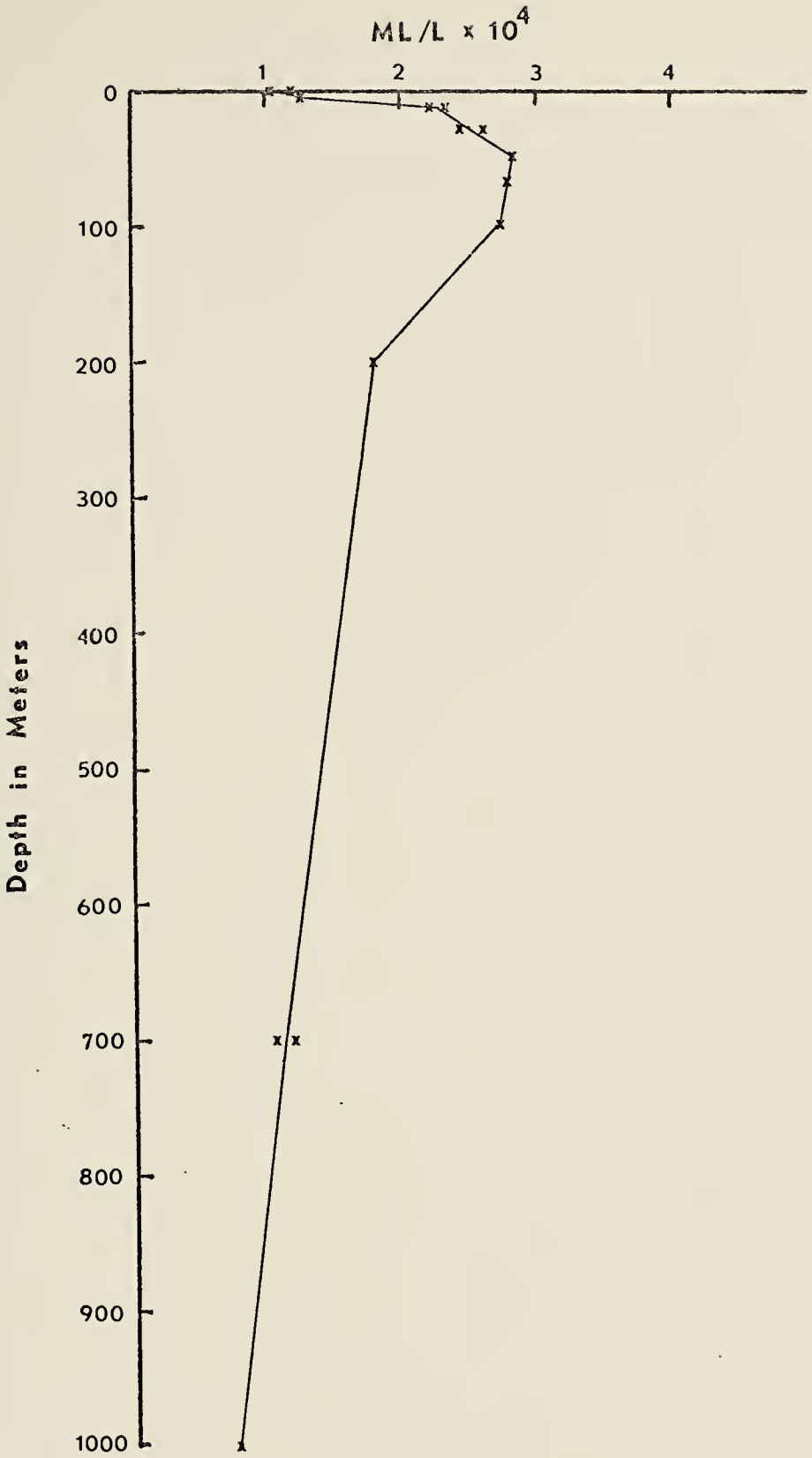

Figure 6. Vertical distribution of CH_4 at the Deep Ocean Station in Monterey Canyon.

Table 2

Methane Concentrations in Monterey Canyon

Depth (meters)	Methane Concentration (ml/l)
0	1.013×10^{-4}
0	1.184×10^{-4}
5	1.252×10^{-4}
15	2.342×10^{-4}
15	2.205×10^{-4}
30	2.433×10^{-4}
30	2.632×10^{-4}
50	2.847×10^{-4}
75	2.783×10^{-4}
100	2.752×10^{-4}
200	1.797×10^{-4}
200	1.759×10^{-4}
700	1.037×10^{-4}
1000	0.751×10^{-4}

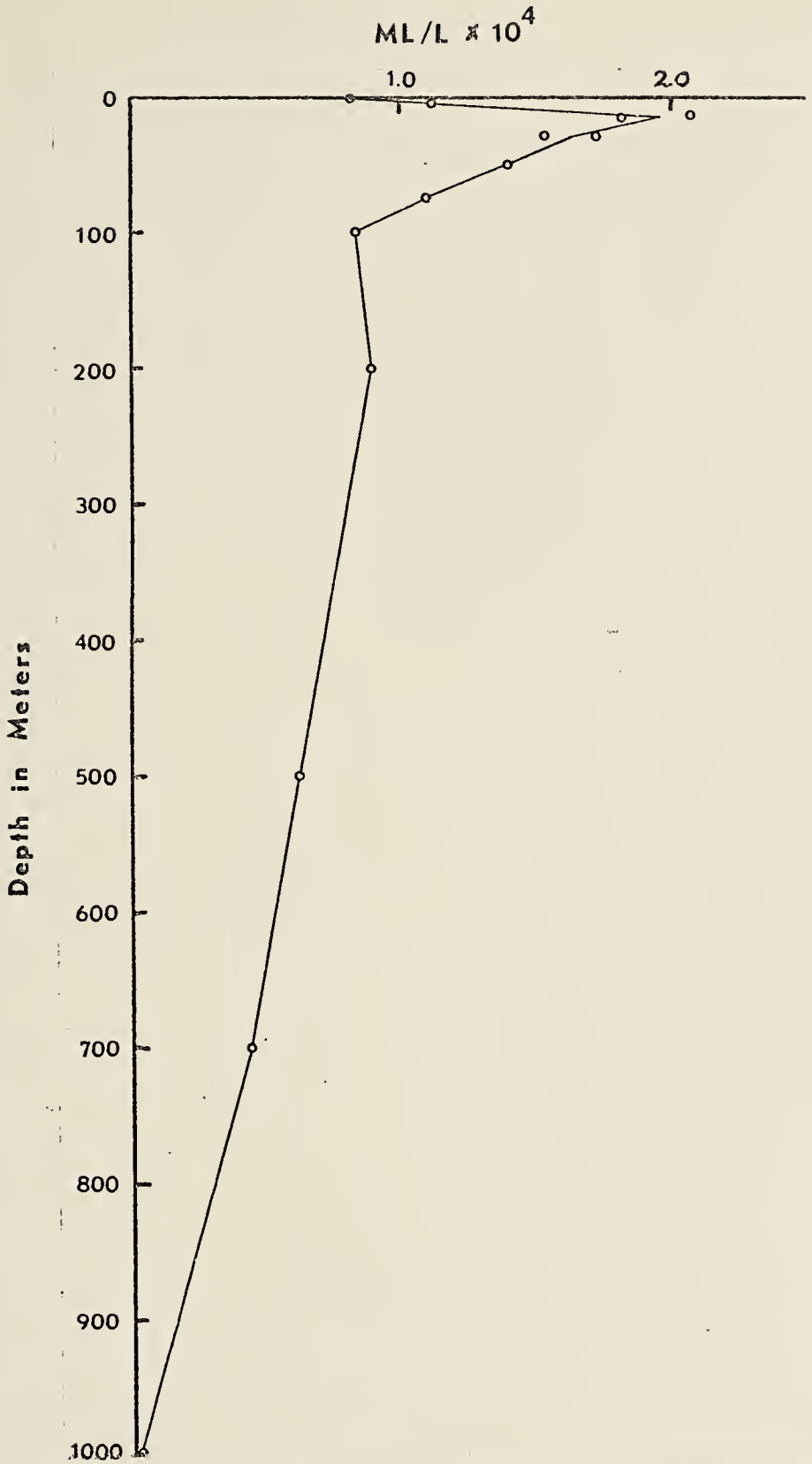

Figure 7. Vertical distribution of CO_2 at the Deep Ocean Station in Monterey Canyon.

Table 3

Carbon Monoxide Concentrations in Monterey Canyon

Depth (meters)	Carbon Monoxide Concentration (ml/l)
0	0.793×10^{-4}
0	0.836×10^{-4}
5	1.230×10^{-4}
15	2.144×10^{-4}
15	1.818×10^{-4}
30	1.522×10^{-4}
30	1.729×10^{-4}
50	1.391×10^{-4}
75	1.086×10^{-4}
100	0.759×10^{-4}
200	0.836×10^{-4}
200	0.859×10^{-4}
500	0.619×10^{-4}
700	0.436×10^{-4}
1000	trace

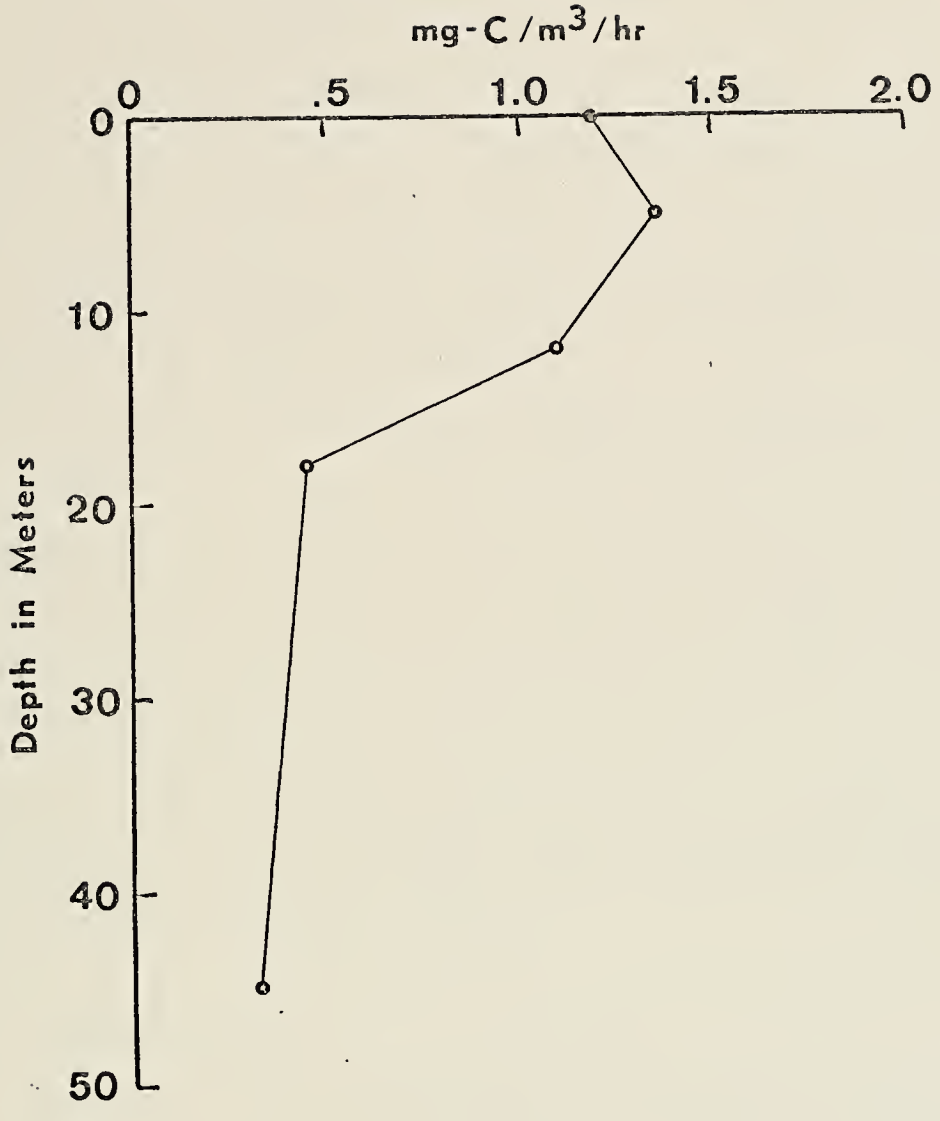

Figure 8. Vertical distribution of Primary Productivity in the upper 50 meters of the Deep Ocean Station in Monterey Canyon (from Rowney, 1973).

are found in Figures 9 through 13 and are tabulated in Tables 4 through 8.

Environmental conditions were as follows. The period prior to 31 October 1972 had been clear for several weeks. During the periods 4-17 November and 3-8 December 1972, overcast skies with heavy rains were predominant. The rest of the time, clear skies prevailed. Heavy swell accompanied the periods of rain. This made it impossible to sample stations 3,4, and 5 during these periods, since it was too rough for the forty foot boat. The surface temperature (Figure 14) decreased from 15°C at the start of the study to 10°C at its conclusion.

All five stations showed high methane concentrations on the first day. These values dropped sharply after the onset of the first storm. Following this storm, the concentrations began to rise, but were again decreased after the second storm. Del Monte Beach showed another increase after this second storm that was not noted at the other stations.

Carbon monoxide did not seem to be affected by the rains as much as methane. It was uniformly low at the start of the study with a general increase throughout the time period. Again, Del Monte Beach showed more variability than the other stations.

C. GRADIENT ANALYSIS

The average of all measurements at each nearshore station was computed and plotted (Figure 15). This provided a gradient analysis for comparison with primary productivity, chlorophyll and nutrient analyses (Rowney 1973).

The methane gradient decreased from Del Monte Beach to Point Cabrillo. It then reversed and showed an increase to the highest value at Point Joe.

Carbon monoxide showed a different pattern. It alternated between decreasing and increasing gradients with a slight overall trend towards higher concentrations at Point Joe.

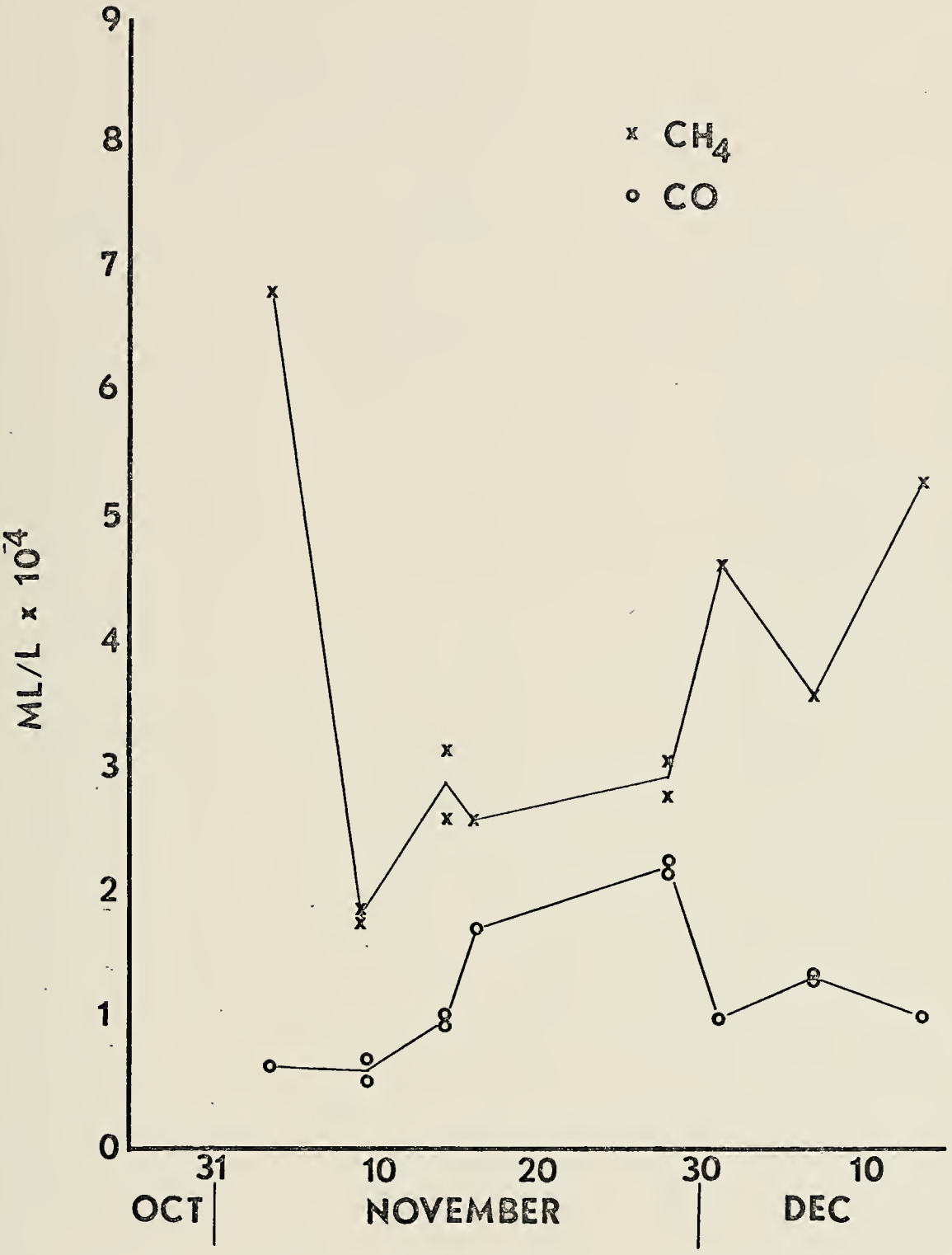

Figure 9. CH_4 and CO concentrations in the surface waters at Del Monte Beach.

Table 4

Methane and Carbon Monoxide

Concentrations at Del Monte Beach

Date	Methane (ml/l)	Carbon Monoxide (ml/l)
11-03-72	6.829×10^{-4}	0.663×10^{-4}
11-09-72	1.842×10^{-4}	0.546×10^{-4}
11-09-72	1.959×10^{-4}	0.735×10^{-4}
11-14-72	2.648×10^{-4}	0.990×10^{-4}
11-14-72	3.187×10^{-4}	1.088×10^{-4}
11-16-72	2.631×10^{-4}	1.763×10^{-4}
11-28-72	3.102×10^{-4}	2.208×10^{-4}
11-28-72	2.837×10^{-4}	2.318×10^{-4}
12-01-72	4.682×10^{-4}	1.039×10^{-4}
12-07-72	3.669×10^{-4}	1.408×10^{-4}
12-07-72	3.547×10^{-4}	1.345×10^{-4}
12-14-72	5.358×10^{-4}	1.046×10^{-4}
12-14-72	5.277×10^{-4}	1.082×10^{-4}

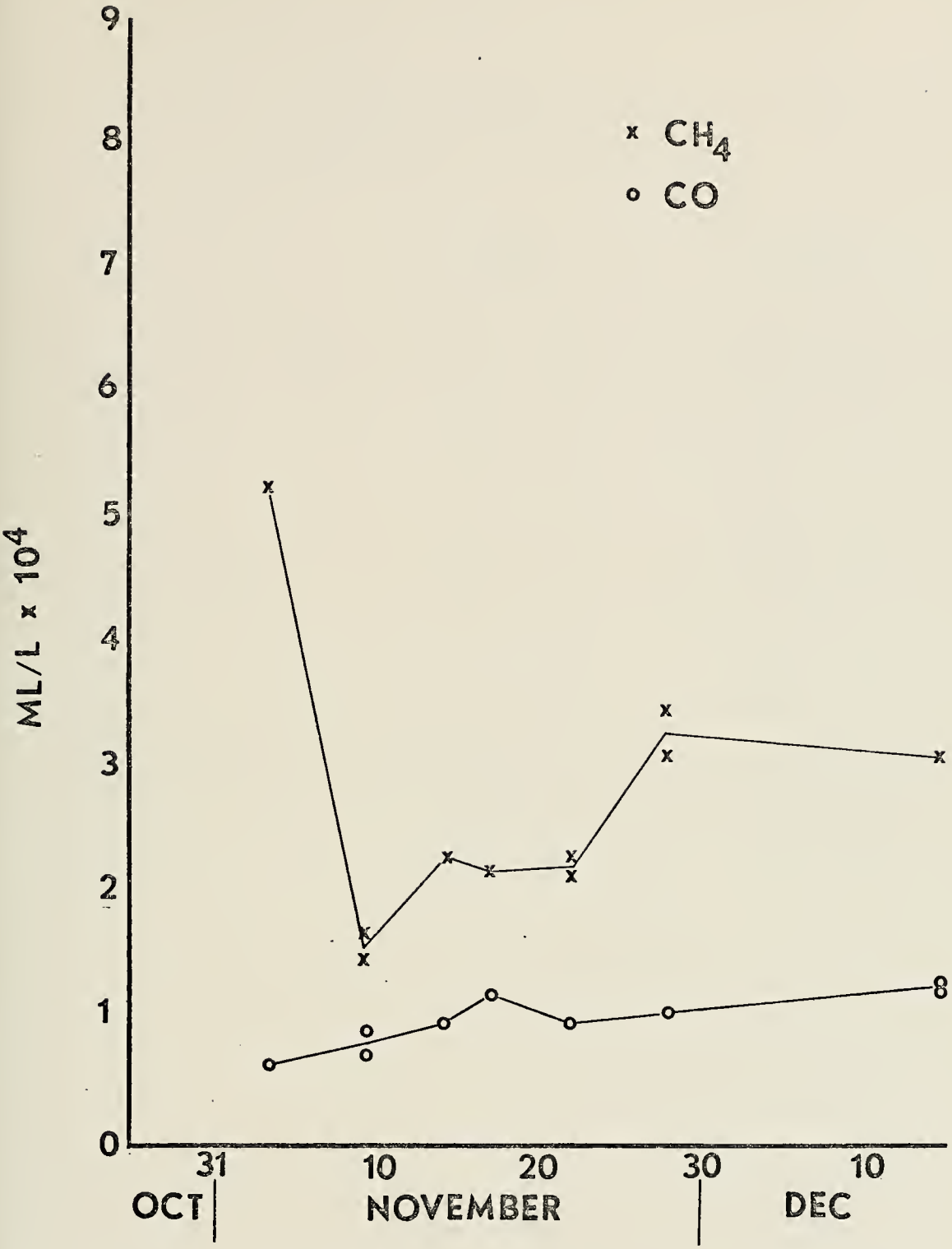

Figure 10. CH_4 and CO concentrations in the surface waters at Point Cabrillo.

Table 5

Methane and Carbon Monoxide

Concentrations at Point Cabrillo

Date	Methane (ml/l)	Carbon Monoxide (ml/l)
11-03-72	5.273×10^{-4}	0.677×10^{-4}
11-09-72	1.714×10^{-4}	0.942×10^{-4}
11-09-72	1.499×10^{-4}	0.733×10^{-4}
11-14-72	2.323×10^{-4}	0.983×10^{-4}
11-17-72	2.219×10^{-4}	1.209×10^{-4}
11-21-72	2.323×10^{-4}	0.955×10^{-4}
11-21-72	2.152×10^{-4}	1.006×10^{-4}
11-28-72	3.106×10^{-4}	1.066×10^{-4}
11-28-72	3.478×10^{-4}	1.097×10^{-4}
12-15-72	3.117×10^{-4}	1.242×10^{-4}
12-15-72	3.096×10^{-4}	1.305×10^{-4}

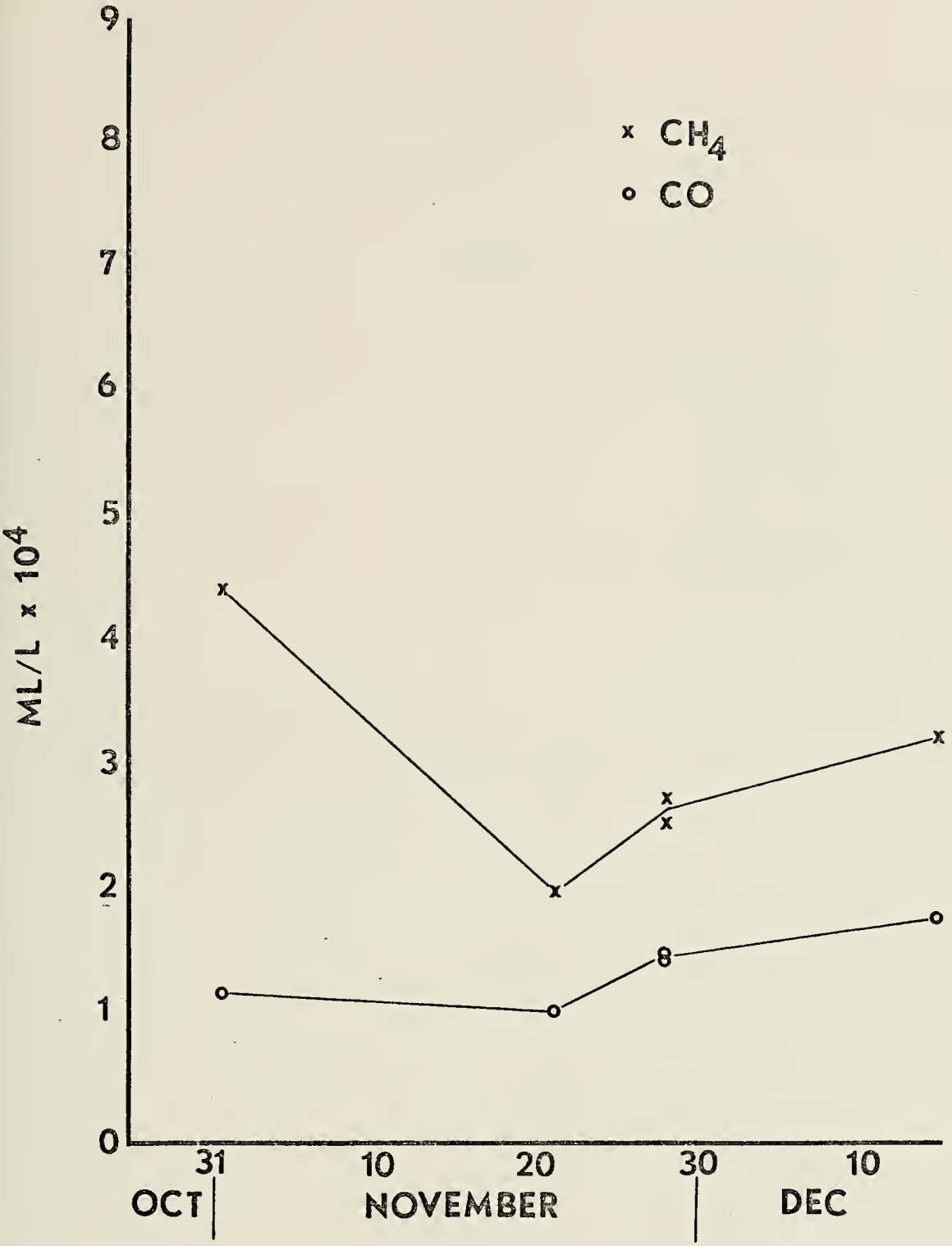

Figure 11. CH_4 and CO concentrations in the surface waters at Point Pinos North.

Table 6

Methane and Carbon Monoxide

Concentrations at Point Pinos North

Date	Methane (ml/l)	Carbon Monoxide (ml/l)
10-31-72	4.437×10^{-4}	1.203×10^{-4}
11-21-72	2.014×10^{-4}	1.085×10^{-4}
11-28-72	2.791×10^{-4}	1.531×10^{-4}
11-28-72	2.587×10^{-4}	1.467×10^{-4}
12-15-72	3.267×10^{-4}	1.833×10^{-4}

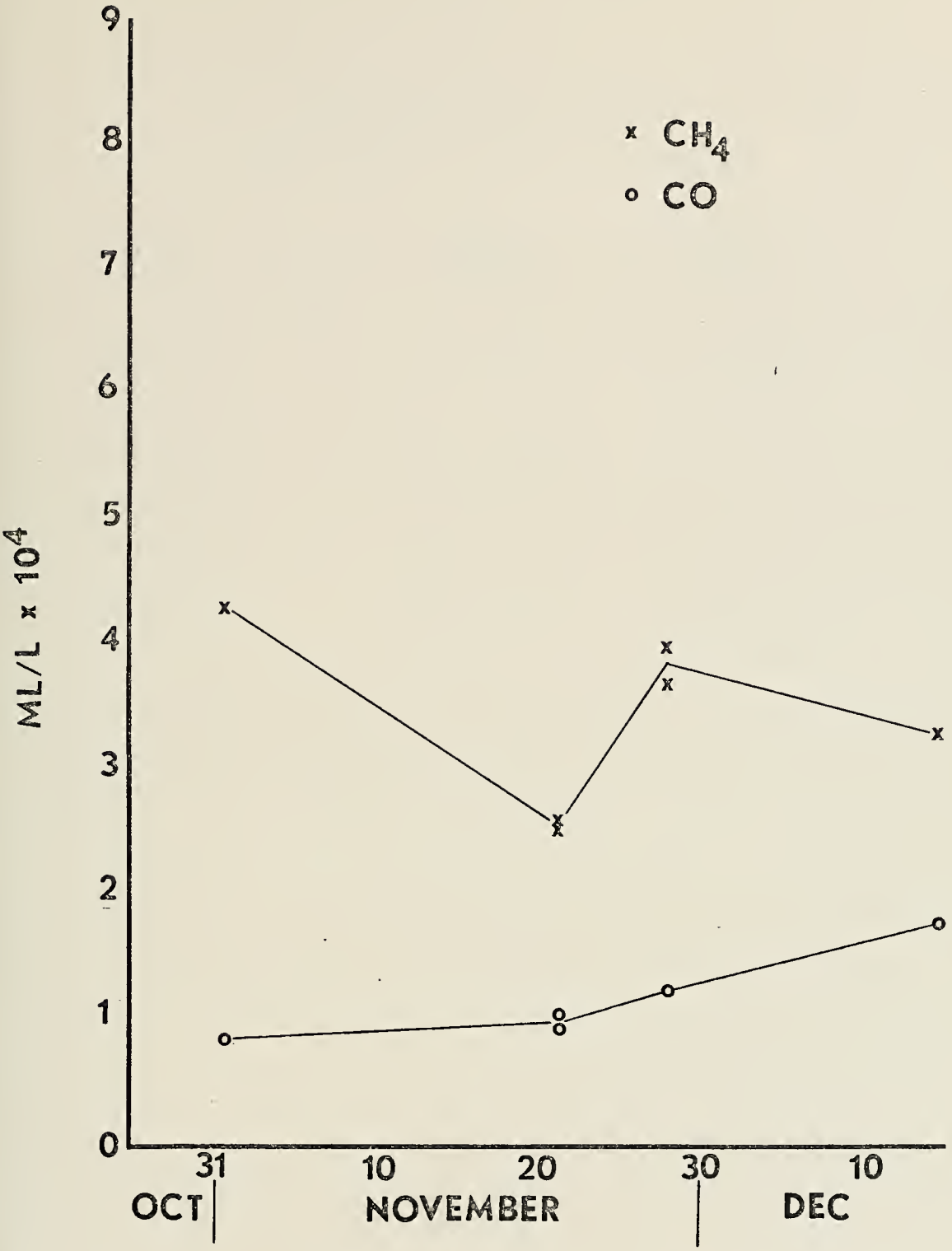

Figure 12. CH_4 and CO concentrations in the surface waters at Point Pinos South.

Table 7

Methane and Carbon Monoxide

Concentrations at Point Pinos South

Date	Methane (ml/l)	Carbon Monoxide (ml/l)
10-31-72	4.317×10^{-4}	0.875×10^{-4}
11-21-72	2.527×10^{-4}	0.952×10^{-4}
11-21-72	2.635×10^{-4}	1.061×10^{-4}
11-28-72	3.998×10^{-4}	1.288×10^{-4}
11-28-72	3.694×10^{-4}	1.251×10^{-4}
12-15-72	3.481×10^{-4}	1.798×10^{-4}

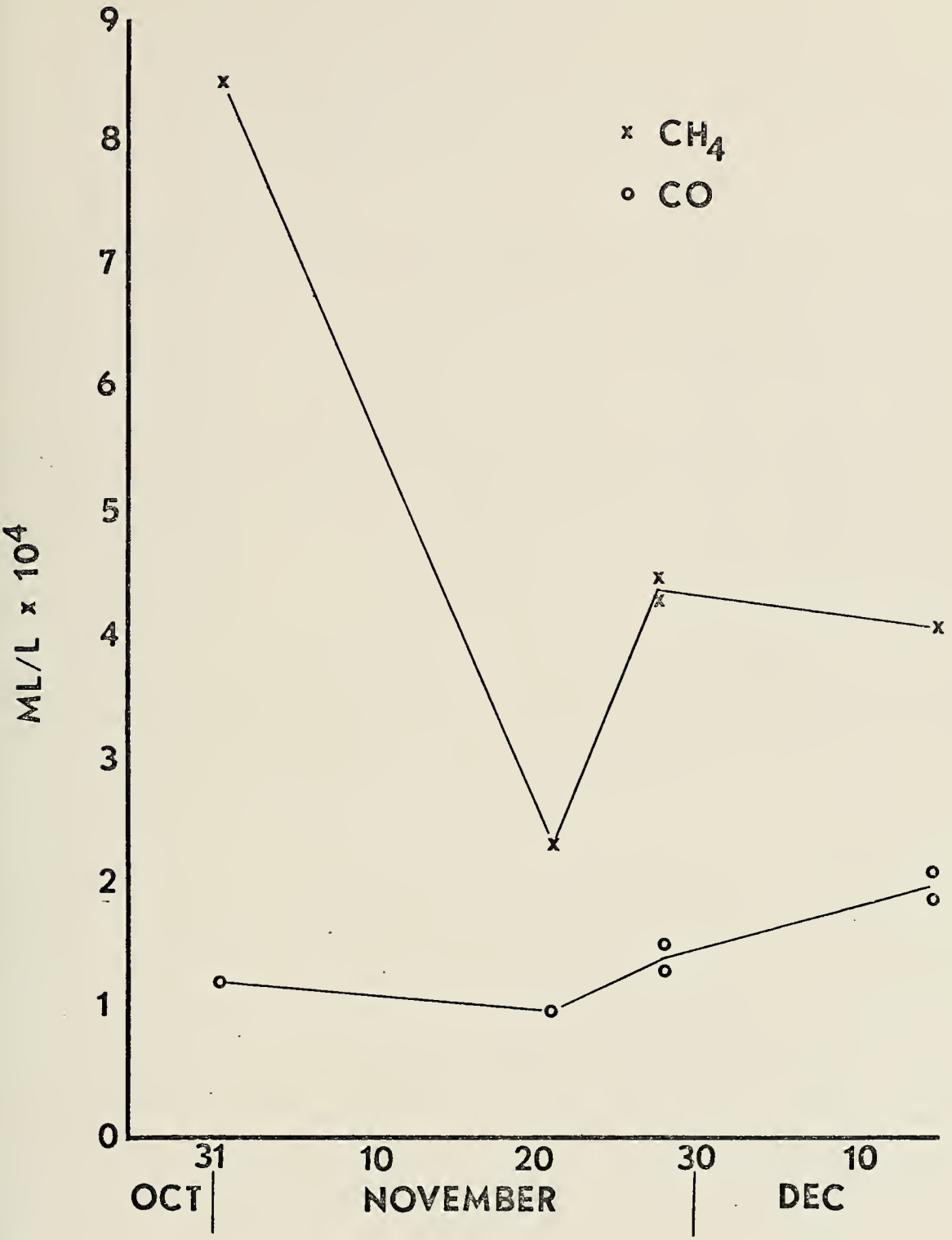

Figure 13. CH_4 and CO concentrations in the surface waters at Point Joe.

Table 8

Methane and Carbon Monoxide

Concentrations at Point Joe

Date	Methane (ml/l)	Carbon Monoxide (ml/l)
10-31-72	8.524×10^{-4}	1.275×10^{-4}
11-21-72	2.300×10^{-4}	1.034×10^{-4}
11-28-72	4.267×10^{-4}	1.548×10^{-4}
11-28-72	4.501×10^{-4}	1.344×10^{-4}
12-15-72	4.088×10^{-4}	2.109×10^{-4}
12-15-72	4.073×10^{-4}	1.903×10^{-4}

Figure 14. Surface temperature.

D. TRANSECTS

The transect across Del Monte Beach proved most interesting. It started 400 yards east of the Monterey sewage disposal plant outfall and proceeded towards the harbor. Figure 16 and Table 9 show the results of this transect. The initial values of methane and carbon monoxide were low and then increased sharply at the "boil" above the outfall. Concentrations dropped back down west of the "boil" and then started to increase again as the stations got closer to Monterey harbor.

The transects from Del Monte Beach to the R-4 buoy (Figure 17 and Table 10) showed a wide variation in concentrations. On 1 December 1972, the methane decreased slightly to the first station beyond the kelp bed and then increased out to the buoy. Carbon monoxide increased slighty beyond the kelp and then remained fairly constant. On 14 December 1972, the methane followed the same pattern, but the drop in concentration from the kelp bed to the first open water station was much greater. Carbon monoxide seemed to decrease slightly beyond the kelp bed and then build up seaward.

The transect from Point Cabrillo to the R-4 buoy (Figure 18 and Table 11) showed very little change in either gas. Methane increased by $.1 \times 10^{-4}$ ml/l from 3.1×10^{-4} ml/l and carbon monoxide decreased $.4 \times 10^{-4}$ ml/l from 1.3×10^{-4} ml/l.

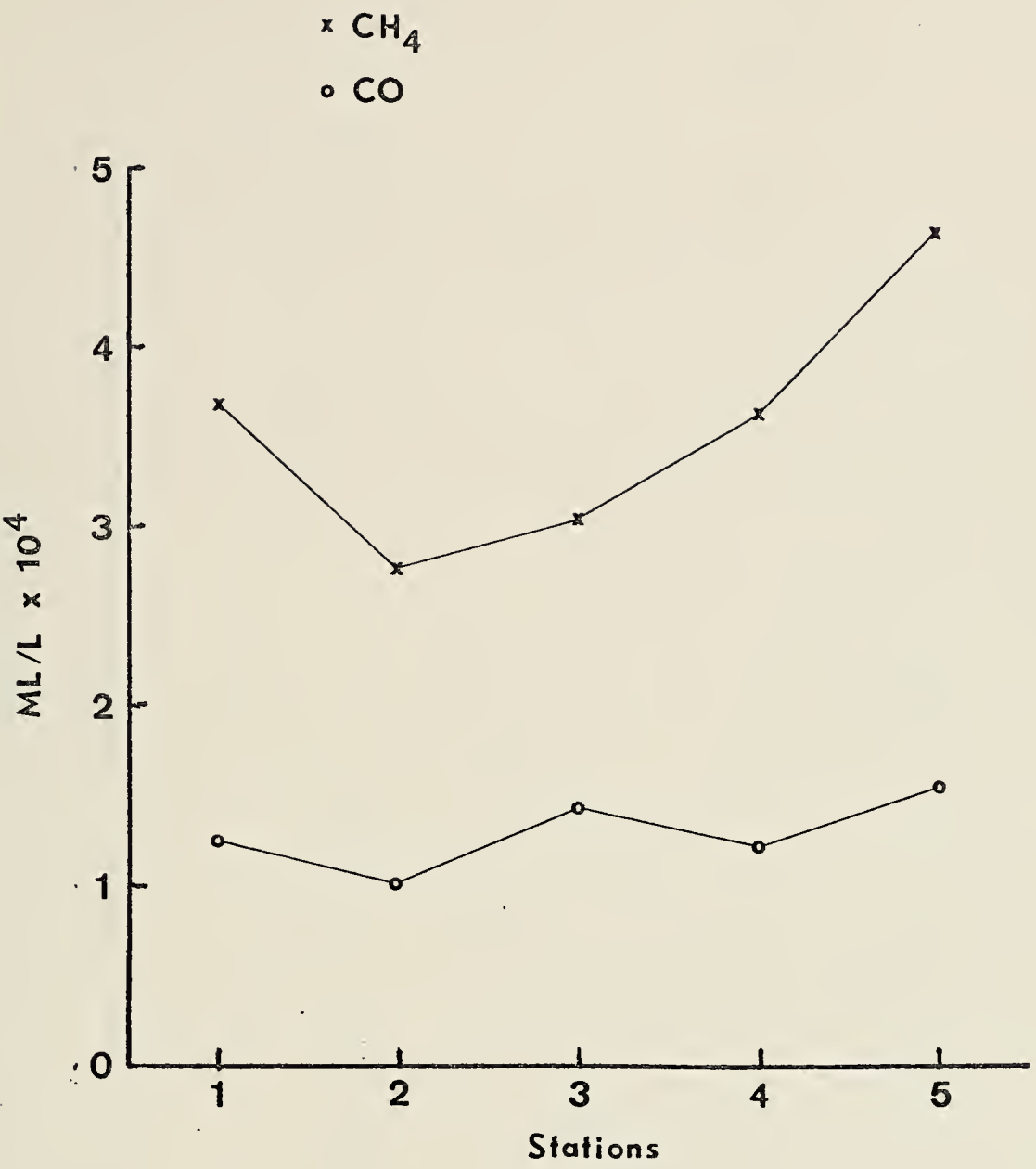

Figure 15. CH_4 and CO gradients between the five nearshore stations.

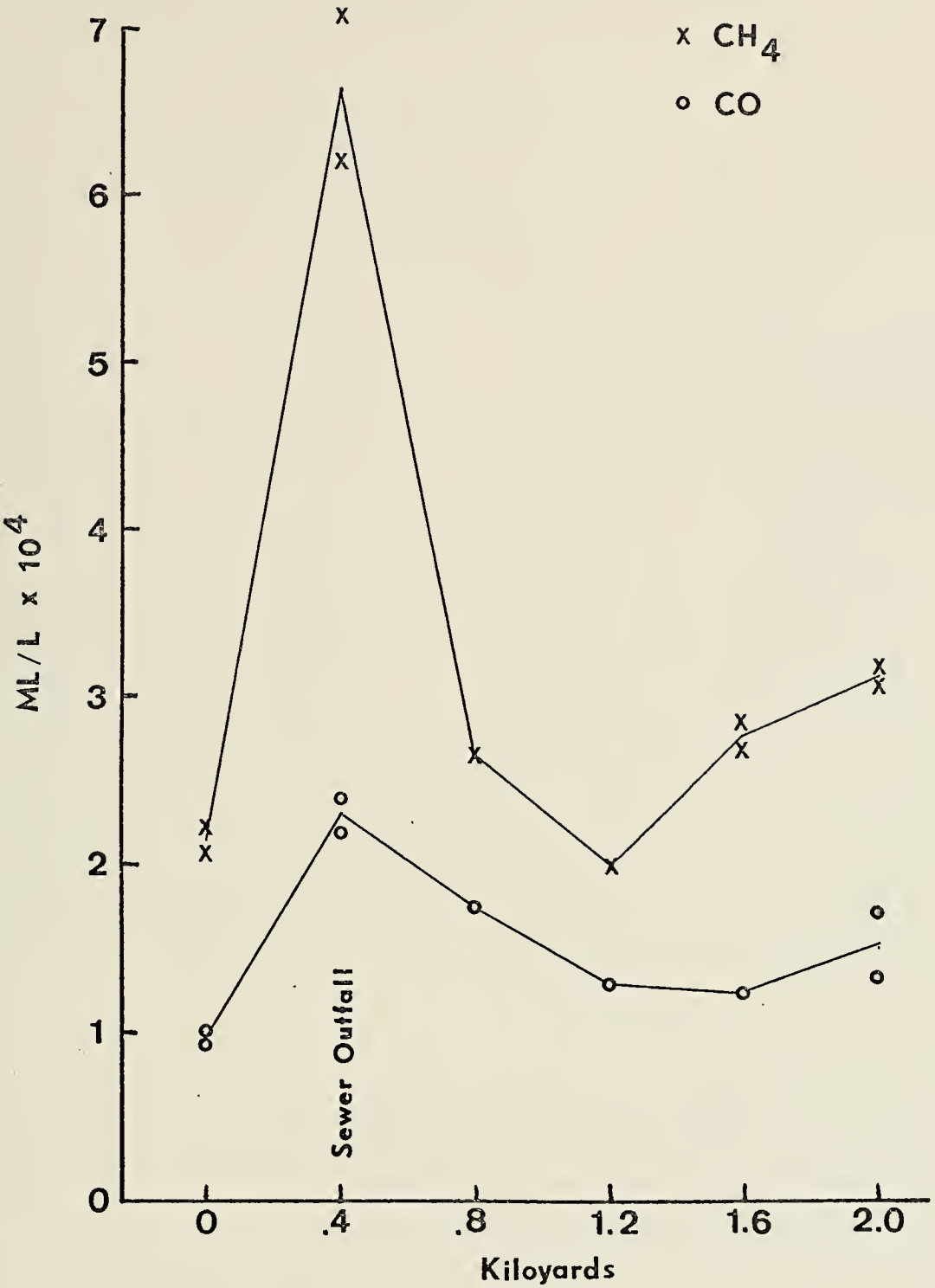

Figure 16. CH_4 and CO concentrations for a transect along Del Monte Beach.

Table 9

Methane and Carbon Monoxide Concentrations for the Transect Along Del Monte Beach

Date	Location	Methane (ml/l)	Carbon Monoxide (ml/l)
11-16-72	Kelp Edge	2.214×10^{-4}	0.935×10^{-4}
11-16-72	Kelp Edge	2.089×10^{-4}	1.040×10^{-4}
11-16-72	Sewer Outfall	7.053×10^{-4}	2.380×10^{-4}
11-16-72	Sewer Outfall	6.198×10^{-4}	2.191×10^{-4}
11-16-72	Pump House	2.631×10^{-4}	1.763×10^{-4}
11-16-72	Beach lab	1.995×10^{-4}	1.276×10^{-4}
11-16-72	Apartments	2.823×10^{-4}	1.222×10^{-4}
11-16-72	Apartments	2.673×10^{-4}	1.241×10^{-4}
11-16-72	Public Beach	3.161×10^{-4}	1.172×10^{-4}
11-16-72	Public Beach	3.054×10^{-4}	3.054×10^{-4}

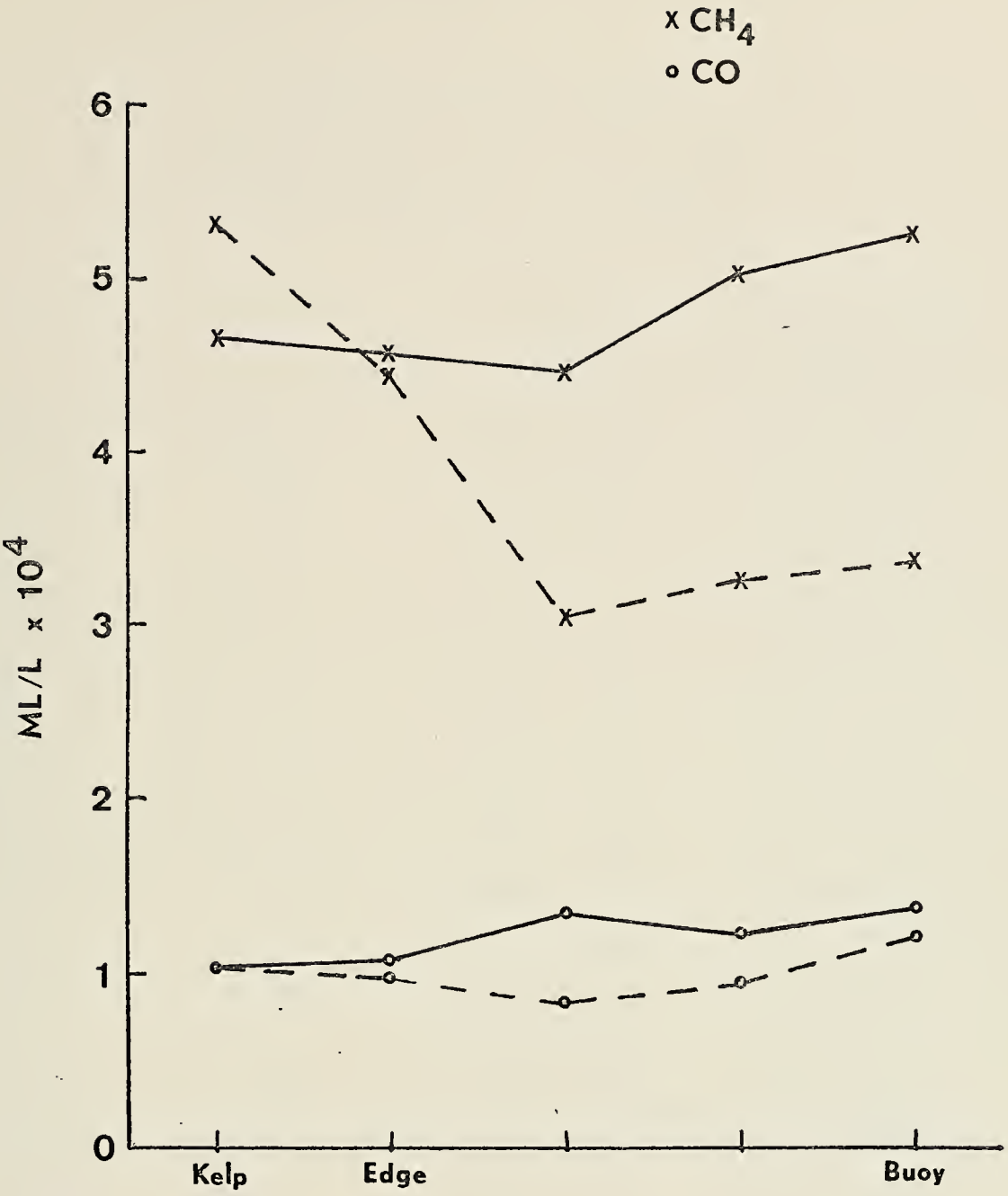

Figure 17. CH_4 and CO concentrations from transects from Del Monte Beach to the R-4 Buoy. Solid line is data for 1 December 1972 and dashed line is data for 14 December 1972.

Table 10

Methane and Carbon Monoxide
Concentrations for the Transect from
Del Monte Beach to the R-4 Buoy

Date	Location	Methane (ml/l)	Carbon Monoxide (ml/l)
12-01-72	Station 1	4.682×10^{-4}	1.039×10^{-4}
12-01-72	Kelp Edge	4.517×10^{-4}	1.041×10^{-4}
12-01-72	Kelp Edge	4.609×10^{-4}	1.080×10^{-4}
12-01-72	Open Water 1	4.490×10^{-4}	1.330×10^{-4}
12-01-72	Open Water 1	4.433×10^{-4}	1.389×10^{-4}
12-01-72	Open Water 2	4.965×10^{-4}	1.272×10^{-4}
12-01-72	Open Water 2	5.105×10^{-4}	1.271×10^{-4}
12-01-72	Station 6	5.287×10^{-4}	1.416×10^{-4}
12-01-72	Station 6	5.233×10^{-4}	1.397×10^{-4}
12-14-72	Station 1	5.358×10^{-4}	1.046×10^{-4}
12-14-72	Station 1	5.277×10^{-4}	1.082×10^{-4}
12-14-72	Kelp Edge	4.374×10^{-4}	0.990×10^{-4}
12-14-72	Kelp Edge	4.594×10^{-4}	1.143×10^{-4}
12-14-72	Open Water 1	2.924×10^{-4}	0.856×10^{-4}
12-14-72	Open Water 1	3.120×10^{-4}	0.854×10^{-4}
12-14-72	Open Water 2	3.277×10^{-4}	0.997×10^{-4}
12-14-72	Station 6	3.382×10^{-4}	1.223×10^{-4}

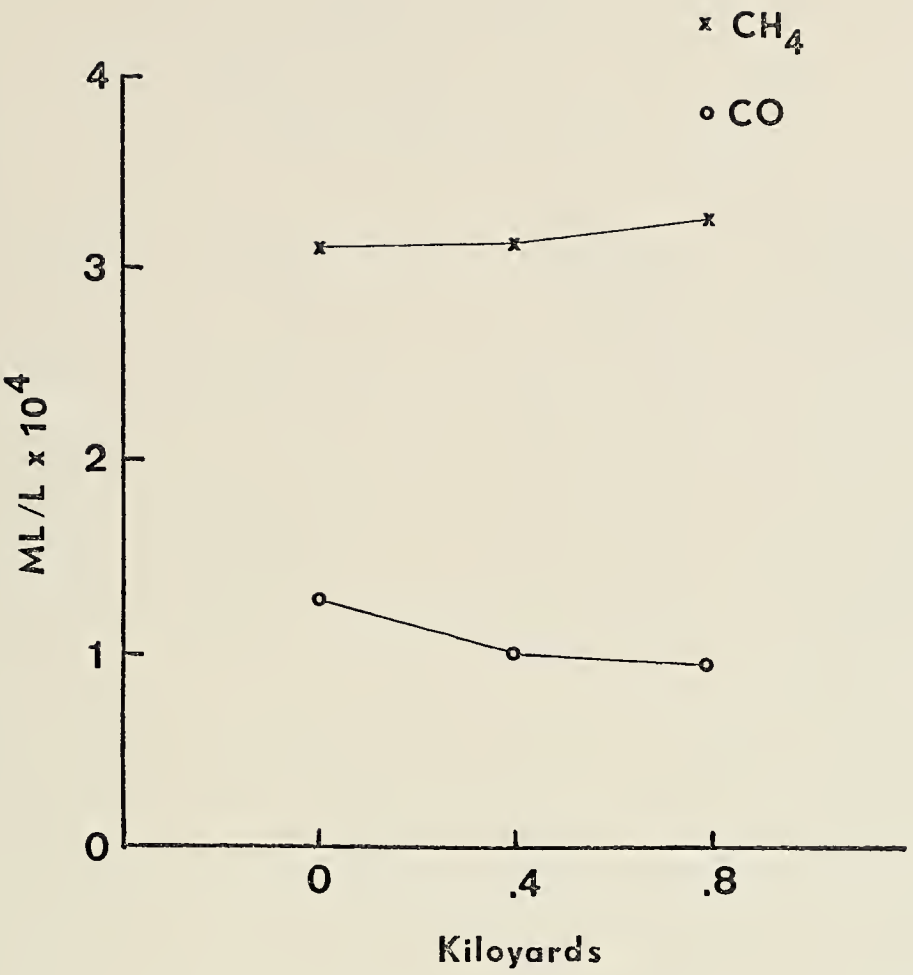

Figure 18. CH_4 and CO concentrations for a transect from Point Cabrillo to the R-4 Bell Buoy.

Table 11

Methane and Carbon Monoxide

Concentrations for the Transect from

Point Cabrillo to the R-4 Buoy

Date	Location	Methane (ml/l)	Carbon Monoxide (ml/l)
12-15-72	Station 2	3.117×10^{-4}	1.242×10^{-4}
12-15-72	Station 2	3.096×10^{-4}	1.305×10^{-4}
12-15-72	Intermediate	3.091×10^{-4}	0.970×10^{-4}
12-15-72	Intermediate	3.136×10^{-4}	1.024×10^{-4}
12-15-72	Station 6	3.231×10^{-4}	0.932×10^{-4}

V. DISCUSSION OF RESULTS

A. PRECISION AND ACCURACY

The precision and accuracy of the gas chromatograph system was checked by running ten consecutive calibration checks. The average of these ten runs was computed as well as the RMS deviation. It was found that to be within plus or minus two RMS deviations, errors as large as 10% could be expected for carbon monoxide and 7.8% for methane.

These errors came mainly from the peak area measurements. First, the determination of a base line proved a problem if there was any drift in the system. To minimize this, the same method of baseline determination was used in each run. This may not eliminate the error, but it should keep it constant.

Area calculation by peak height and width at half height measurement only approximates actual peak area. To solve this problem, either the very careful use of a planimeter, cutting out the peaks and weighing them, or an automatic integrator could be used. These first two unfortunately have the problem of increased analysis time, and the last one, high cost.

B. OPEN OCEAN DEEP STATION

The comparison of Figures 7 and 8 shows a striking correspondence between carbon monoxide concentrations and primary productivity. These results seem to give support to the hypothesis that phytoplankton may be producing carbon monoxide, but this is unexpected and requires experimental verification.

Some anaerobic, methanogenic bacteria are known to convert carbon monoxide to methane (Pine 1971, Jaffe 1970). Figure 19 shows an increase

in both methane and carbon monoxide from the surface to 15 meters. If the carbon monoxide production is related to phytoplankton, and if methane is produced anaerobically *in situ* (or carried there from an anaerobic source) this could explain the concurrent increase of these gases in the surface layer. From 15-100 meters, the carbon monoxide decreases, but the methane continues to increase. This may show continued bacterial conversion of carbon monoxide to methane below the layer of high productivity, or the advection of a methane rich water mass in the upper 100 meters.

Below 100 meters both gases decrease with depth.

C. TEMPORAL STUDY

The temporal study showed a marked difference between the stations in Monterey Bay (Stations 1 and 2) and those on the exposed coast. Station 1 at Del Monte Beach showed great variability in both methane and carbon monoxide (Figure 9). This was expected since there are many more factors affecting these gases in this environment; sewage disposal plant effluent, pollution from Monterey harbor, and city storm sewer outlets all contribute to the water budget of this station. It is interesting to compare the values of primary productivity with the methane concentrations. They both show marked decrease following the onset of the first storm and then both increase throughout the rest of the study. Carbon monoxide does not show any correlation with primary productivity at this station. The cause for the large jump in carbon monoxide concentration during the period 16-28 November 1972 is unknown. It is possible that this variability in concentrations was present at the other stations and that the more frequent sampling of Del Monte Beach merely showed the transient nature of these gases.

Point Cabrillo (Station 2), still being within the confines of the

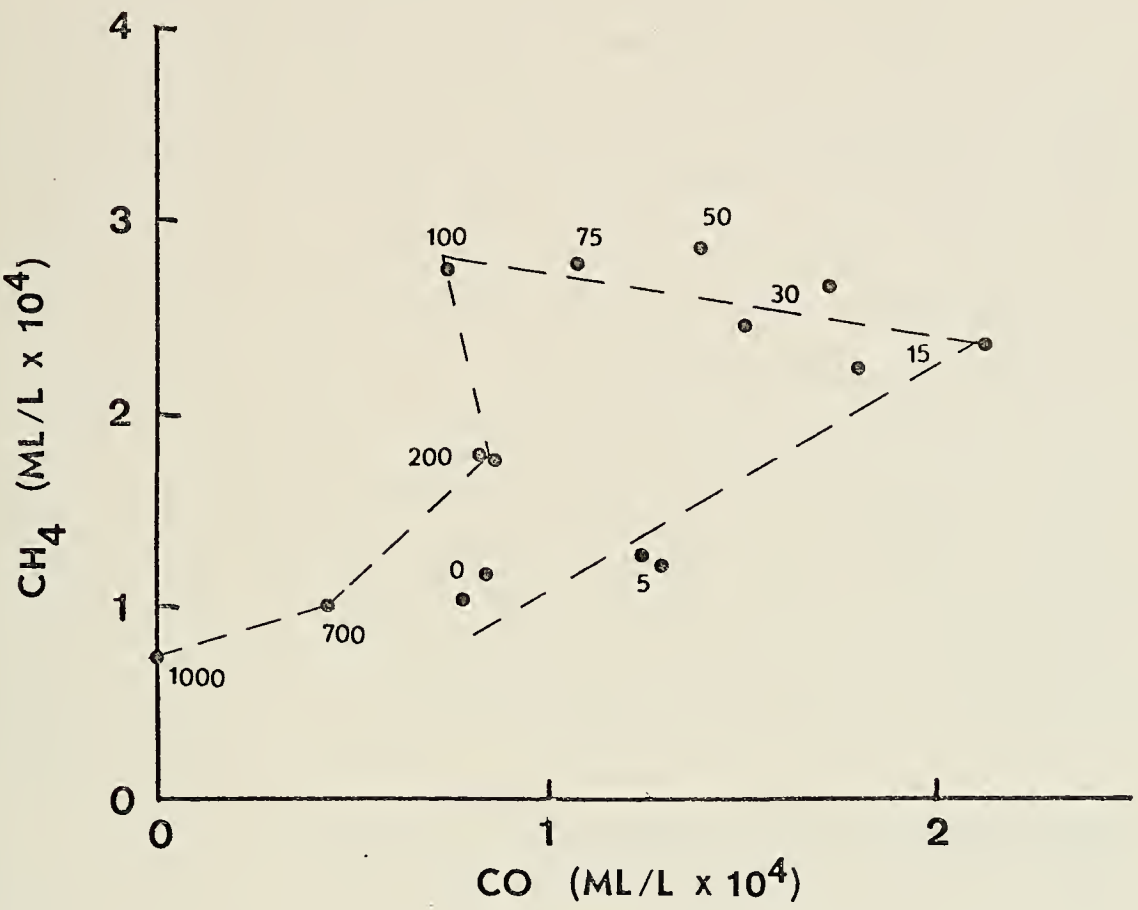

Figure 19. Plot of CH_4 vs. CO in the Deep Ocean Station in the Monterey Canyon. Numbers indicate depth in meters.

bay, had characteristics similar to those found at Del Monte Beach. Since it was further removed from the sources of the pollutants at Del Monte Beach, the variability was not as great. There was still a parallel trend between methane and primary productivity, and none noted for carbon monoxide.

Station 3 at Point Pinos North is subject to the heavy surf action from oceanic waves. Like stations 1 and 2, it, too, showed close correlation between methane and primary productivity, but it also showed a trend between carbon monoxide and primary productivity after the heavy rains.

Station 4 was located just off the Pacific Grove sewage disposal plant outfall at Point Pinos. Here, the methane-primary productivity and the post storm carbon monoxide-primary productivity correlations were both good. It was interesting to note that little or no influence from the sewage effluent was noted in the kelp bed off shore, while the rocks near the outfall appeared to be devoid of life. This probably shows the diluting effect on the heavily chlorinated sewage of the turbulent mixing from the surf in this area.

Station 5 at Point Joe initially showed exceptionally high methane concentrations. Following the first storm, this was reduced to values comparable to the other four stations. Following the rains, it increased more rapidly than any other station. These high methane concentrations seem to indicate a methane source near Point Joe. It is very possible that this source is the Pebble Beach sewage outfall, located just south of Point Joe, where apparently untreated sewage is dumped directly into the ocean.

When the methane concentration was exceptionally high, primary productivity was low. This does not follow the pattern set by the other four

stations. It is possible that phytoplankton growth is inhibited when methane concentrations reach a certain toxic level, or both may be affected by a third factor. After the rains, and subsequent decrease in methane concentrations, the correlation between methane and primary productivity was again apparent.

Carbon monoxide and primary productivity showed very good correlations throughout the sampling period at this station.

D. GRADIENT ANALYSIS

The gradient analysis (Figure 15) indicates the possibility of methane sources at Del Monte Beach and Point Joe. Since the high methane gradients exist at or near sewage disposal plant outfalls, this supports the hypothesis that methane can be used as a tracer for sewage effluent.

The carbon monoxide gradient was not as dramatic as that for methane. It also showed the highest value at Point Joe. An examination of the plant population of Point Joe may help explain this. Stations 1 through 4 are predominantly Macrocystis pyrifera while station 5 is mainly Nereocystis leutkeana. Loewus and Delwiche (1963) have shown that Nereocystis leutkeana produces three times as much carbon monoxide as Macrocystis pyrifera. Therefore, one would expect higher carbon monoxide concentrations at Point Joe than at other stations. A closer examination of the macroalgae at each station might help to explain the variation in the carbon monoxide gradients.

The open ocean value of 1.1×10^{-4} ml/l measured in the Monterey Canyon is 2.4 times the equilibrium concentration of methane in seawater (assuming methane content of air is 1.24 ppm). Similarly, the carbon monoxide concentration of 0.81×10^{-4} ml/l is 22.5 times the equilibrium concentration (assuming the highest reported oceanic partial pressure for

carbon monoxide of 0.17 ppm). The average concentration for both carbon monoxide and methane at each station was considerably higher than the oceanic value. Therefore, it is likely that these kelp beds are sources of these gases to the atmosphere.

E. TRANSECTS

The transects from Del Monte Beach to the R-4 buoy showed the effect of the rains on these gases. Before the rains, the concentrations of both gases in the kelp bed and in the open water were high. After the rains, the values in the kelp were high, but the open water values were decreased substantially. This may show the effect of the kelp as an inhibitor to the mixing process.

The transect from Point Cabrillo to the R-4 buoy showed essentially constant, low methane concentrations. This transect was taken after the rains, and since no methane source near Point Cabrillo was indicated in the gradient analysis, this type of profile could be expected.

The carbon monoxide, on the other hand, showed a decrease seaward. If, indeed, the macroalgae are producing carbon monoxide, this decrease away from the kelp bed could be expected.

Since the gradient analysis indicated a source of methane at Del Monte Beach, a transect was taken there to determine the source of the pollutant (Figure 16). As was expected, extremely high methane values were found in the "boil" above the sewage outfall. Since Monterey does not use an anaerobic treatment process, the source of this methane raised an interesting question.

One possibility was that organic matter was settling out around the outfall. This could create anaerobic conditions and thus generate high concentrations of methane. This idea was abandoned after talking with divers who had frequented the area.

The second premise was that the methane was already present before the sewage reached the treatment plant. This was substantiated by some early attempts to analyze tap water. The city water had so much methane in it that the electrometer in the gas chromatograph was immediately saturated and no value could be obtained.

There was also an indication that the harbor was also a source of both carbon monoxide and methane. With the leakage of petroleum products and the exhaust from power boats, it is no wonder that this was observed.

VI. SUMMARY

Results from the open ocean station and several nearshore stations show a possible correlation between carbon monoxide and primary productivity in this relatively pollution-free environment. Methane was also shown to be present in the upper 100 meters, showing a maximum at about 50 meters. This may indicate biological production of this gas in an oxygen rich environment.

At the nearshore stations, concentrations of methane and carbon monoxide were both far above equilibrium and open ocean values. It was shown that methane concentrations were highest in the vicinity of sewage outfalls and that the source of this gas may be the city water supply. Carbon monoxide concentrations may very well be dependent on the type of plant life in the surrounding waters.

Rain was shown to act as a depressant for methane concentrations and primary productivity, but had little effect on carbon monoxide. Methane in very high concentrations appeared to act as a poison to phytoplankton since primary productivity dropped dramatically in methane rich waters.

The transects showed that methane was an effective tracer for sewage disposal plant effluent and that the kelp seemed to slow the diffusion and mixing of pollutants.

From equilibrium considerations, the waters of Monterey Bay were found to be supersaturated with carbon monoxide and methane. The highest concentrations were, for the most part, located in the kelp beds. These results indicate that, at least locally, the ocean is a source of carbon monoxide and methane in the atmosphere.

VII. RECOMMENDATIONS

Further work with this system could prove valuable in the field of air-sea interaction. By incorporating an air sampling loop, direct measurements of interfacial gradients for a variety of components could be made. It would have been especially helpful in the present study to have known the atmospheric concentrations of these gases.

Due to the limitations of the gas chromatograph used, the hydrocarbons higher than methane that were trapped were not analyzed. In the future, a useful addition to the system would be a dual channel, dual detector gas chromatograph. This would allow simultaneous analysis of a wide variety of organics. The addition of a self-integrating recorder would provide the capability of making on-station, real-time measurements of these dissolved gases.

It is recommended that further work on carbon monoxide and methane be pursued in the Monterey Submarine Canyon. Paucity of ship time aboard R/V Acania precluded further investigation of this area during this study.

APPENDIX A

Analysis Procedures

Sample Transfer

1. Bottle on.
2. Open drain valve to sample bottle to remove old sample from line.
3. Turn drain valve to fill stripping chamber.
4. Turn transfer valve.
5. At 100 ml. turn off transfer valve.
6. Turn drain valve off at zero.
7. Open pressure release and close again.

Stripping

1. Place cold traps.
2. Valve T1 to Trap.
3. Valve T2 to Trap.
4. Trap/Anal valve to Trap.
5. Cal valve to Cal Fill.
6. Trap/Bypass to Trap.
7. Open trap isolation valves.
8. Ensure cap is on valve T1.
9. Open helium purge and start timer.
10. Turn on magnetic stirring bar.
11. Check exhaust flow (13).
12. Close trap isolation valves at 720 sec.
13. Drain 25 - 50 ml. from chamber.

14. Switch Trap/Bypass valve to Bypass.

15. Leave helium flow on.

Analysis

1. Remove cold traps.
2. Place hot water on Trap 2.
3. Warm for one minute.
4. Place Trap/Anal valve to Anal.
5. Set range and attenuation.
6. Zero recorder using Bucking Voltage (obtain baseline).
7. Turn recorder on Low (1"/min.)
8. Turn valve T2 to anal at reference line on recorder.
9. Analysis is complete in seven minutes.

Clean up

1. Drain stripping chamber to about 475 ml.
2. Turn off purge helium.
3. Drain to 500 ml.
4. Place hot water on Trap 1.
5. Remove cap from T1.
6. Switch T1 to Anal.
7. Warm for 1 minute.
8. Repalce cap on T1.
9. Remove hot water.
10. Remove sample bottle.

APPENDIX B

Procedures for Blanks and Calibrations

Calibration (direct injection)

Valve T1 - Trap position.

Valve T2 - Trap position

Anal/Trap - Trap position

Cal valve - Cal Fill position

Trap/Bypass - Bypass position
Fill cal loop
Cal valve - Cal inj. position

Calibration (through traps)

Valve T1 - Trap position

Valve T2 - Trap position

Anal/Trap - Anal position

Cal valve - Cal Fill position

Trap/Bypass - Trap position

Fill Cal Loop

Cal valve - Cal inj. position

Run as if it were a sample, follow stripping and analysis procedure as in Appendix A.

Blank (Run before a series of samples)

Valve T1 - Trap position

Valve T2 - Trap position

Trap/Bypass - Trap position

Cal valve - not important

Run degassed sample, follow stripping and analysis procedures in Appendix A to clear system or check for purge gas contamination.

Appendix C

Program for Computing Concentrations

```
      DIMENSION H(2),CH(2),W(2),CW(2),A(2),CA(2),CV(2),VOL(2),CONC(2),
     1COUNT(2),CCOUNT(2),LOC(5),X(30),Y(30),DEPTH(30)
      CV(1)=70.3E-6
      CV(2)=71.1E-6
      J=1
      K=1000
      WRITE (6,102)
  102 FORMAT (T12,'DATE',12X,'LOCATION',12X,'BOTT. NO.',12X,'DEPTH',12X,
     1'METHANE',12X,'CARBON MONOXIDE',//)
 1000 READ (5,100,END=9999) IDATE,IBOT,LOC,I,IDEPTH,CH(I),CW(I),CRNG,
     1CATT,H(I),W(I),RNG,ATT,SAMP
  100 FORMAT (I6,I4,5A4,I1,I4,8F5.0,F5.3)
      A(I)=H(I)*W(I)
      CA(I)=CH(I)*CW(I)
      COUNT(I)=A(I)*RNG*ATT
      CCOUNT(I)=CA(I)*CRNG*CATT
      VOL(I)=(CV(I)*COUNT(I))/(CCOUNT(I))
      CONC(I)=VOL(I)/SAMP
      IF (I.EQ.1) GO TO 1000
      WRITE (6,101)IDATE,LOC,IBOT,IDEPTH,CONC(1),CONC(2)
  101 FORMAT ('0',T11,I6,T22,5A4,T50,I4,T69,I4,T85,1PE10.3,T107,1PE10.3)
      GO TO 1000
 9999 STOP
      END
```

DISSOLVED GASES DATA SHEET

Raw Data

VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST
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	1		2	0	1399.	844.	1.0	2.0	2029.	903.	1.0	1.0	.500
	2		1	0	2397	477	1.0	2.0	2198.	494.	1.0	8.0	.500
	2		2	0	1309.	844	1.0	2.0	1519.	1031.	1.0	1.0	.500
	3		1	0	2397.	477	1.0	2.0	—	—	1.0	8.0	.500
	3		2	0	1309.	844	1.0	2.0	—	—	1.0	1.0	.500
	4		1	0	2397.	477	1.0	2.0	2946.	524.	1.0	8.0	.500
	4		2	0	1309.	844.	1.0	2.0	1033.	1918.	1.0	1.0	.500
	1	DEL MONTE BEACH	1	0	2397.	477.	1.0	2.0	2717.	511.	1.0	8.0	.500
	1		2	0	1309.	844.	1.0	2.0	1189.	866.	1.0	1.0	.500
	2		1	0	2397.	477.	1.0	2.0	2347.	481.	1.0	8.0	.500
	2		2	0	1309.	844.	1.0	2.0	—	—	1.0	1.0	.500

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DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

R.V. ACANIA	9	07 1100 NOV 72	08 2030 NOV 72	JTWilcox
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

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11 9 72	1	MONTEREY CANYON	1	1200	2612.	465.	1.0	2.0	—	—	1.0	2.0	.500
	1		2	1900	1638.	736.	1.0	2.0	—	—	1.0	1.0	.500
	2		1	1900	2612.	465.	1.0	2.0	661.	491.	1.0	4.0	.500
	2		2	1900	1638.	736.	1.0	2.0	999.	999.	1.0	1.0	.500
	3		1	700	2612.	465.	1.0	2.0	2650.	491.	1.0	1.0	.500
	3		2	700	1638.	736.	1.0	2.0	951.	778.	1.0	1.0	.500
	4		1	700	2612.	465.	1.0	2.0	1265.	469.	1.0	1.0	.500
	4		2	700	1638.	736.	1.0	2.0	1509.	766.	1.0	1.0	.500
	5		1	500	2612.	465.	1.0	2.0	—	—	1.0	4.0	.500
	5		2	500	1638.	736.	1.0	2.0	1409.	758.	1.0	1.0	.500
	6		1	500	2612.	465.	1.0	2.0	2670.	472.	1.0	4.0	.500
	6		2	500	1638.	736.	1.0	2.0	2828.	763.	1.0	1.0	.500
	7		1	200	2612.	465.	1.0	2.0	893.	473.	1.0	8.0	.500
	7		2	200	1638.	736.	1.0	2.0	2018.	722.	1.0	1.0	.500
	8		1	200	2612.	465.	1.0	2.0	1617.	480.	1.0	4.0	.500
	8		2	200	1638.	736.	1.0	2.0	1924.	737.	1.0	1.0	.500
	9		1	100	2612.	465.	1.0	2.0	—	—	1.0	4.0	.500
	9		2	100	1638.	736.	1.0	2.0	—	—	1.0	1.0	.500
	10		1	100	2612.	465.	1.0	2.0	1238.	469.	1.0	8.0	.500
	10		2	100	1638.	736.	1.0	2.0	1637.	786.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

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111772	1.1	MONTEREY CANYON	1	75	24667.	4882.	1.0	4.0	72228.	5228.	1.0	4.0	.500
	1.1		2	75	15299.	7558.	1.0	2.0	5443.	8155.	1.0	4.0	.540
	1.2		1	75	24667.	4882.	1.0	2.0	24023.	5540.	1.0	4.0	.500
	1.2		2	75	15299.	7558.	1.0	2.0	39943.	7993.	1.0	1.0	.500
	1.3		1	50	24667.	4882.	1.0	2.0	21777.	5553.	1.0	4.0	.500
	1.3		2	50	15299.	7558.	1.0	2.0	13883.	8220.	1.0	2.0	.520
	1.4		1	50	24667.	4882.	1.0	2.0	29177.	5523.	1.0	4.0	.500
	1.4		2	50	15299.	7558.	1.0	2.0	23331.	7721.	1.0	2.0	.500
	1.5		1	30	24667.	4882.	1.0	2.0	41024.	5205.	1.0	8.0	.500
	1.5		2	30	15299.	7558.	1.0	2.0	18523.	7761.	1.0	2.0	.500
	1.6		1	30	24667.	4882.	1.0	2.0	31098.	4888.	1.0	4.0	.500
	1.6		2	30	15299.	7558.	1.0	2.0	15590.	7805.	1.0	2.0	.500
	1.7		1	15	24667.	4882.	1.0	2.0	19155.	4887.	1.0	4.0	.500
	1.7		2	15	15299.	7558.	1.0	2.0	18880.	7888.	1.0	2.0	.500
	1.8		1	15	24667.	4882.	1.0	2.0	19334.	5112.	1.0	4.0	.500
	1.8		2	15	15299.	7558.	1.0	2.0	22881.	7666.	1.0	2.0	.500
	1.9		1	5	24667.	4882.	1.0	2.0	18886.	5188.	1.0	4.0	.500
	1.9		2	5	15299.	7558.	1.0	2.0	25776.	7688.	1.0	2.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

K.V. Acania	7	071100 NOV 72	101700 NOV 72	JTWelch
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMB	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
1 2 3 4 5 6	7 8 9 10	11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	31	32 33 34 35	36 37 38 39 40	41 42 43 44 45	46 47 48 49 50	51 52 53 54 55	56 57 58 59 60	61 62 63 64 65	66 67 68 69 70	71 72 73 74 75	76 77 78 79 80
111772	20	MONTEREY CANYON	1	5	2367.	442.	1.0	2.0	765.	609.	1.0	4.0	.500
	20		2	5	1412.	236.	1.0	2.0	2048.	878.	1.0	1.0	.500
	21		1	0	2313.	464.	1.0	2.0	843.	536.	1.0	4.0	.500
	21		2	0	1476.	250.	1.0	2.0	1640.	794.	1.0	1.0	.500
	22		1	0	2154.	461.	1.0	2.0	1429.	513.	1.0	2.0	.500
	22		2	0	1395.	219.	1.0	2.0	1457.	768.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

'10' Boat	10	09:30 Nov 72	09:400 Nov 72	Student
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
1 2 3 4 5 6	7 8 9 10	11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	31	32 33 34 35	36 37 38 39 40	41 42 43 44 45	46 47 48 49 50	51 52 53 54 55	56 57 58 59 60	61 62 63 64 65	66 67 68 69 70	71 72 73 74 75	76 77 78 79 80
1.1.09.72	1	HOPKINS MARINE STA	1	0	3358.	491.	1.0	2.0	519.	692.	1.0	8.0	.500
	1		2	0	1513.	752.	1.0	2.0	1379.	1190.	1.0	1.0	.500
	2		1	0	3358.	491.	1.0	2.0	605.	519.	1.0	8.0	.500
	2		2	0	1513.	752.	1.0	2.0	1460.	893.	1.0	1.0	.500
	3	DEL MONTE BEACH	1	0	3358.	491.	1.0	2.0	734.	517.	1.0	8.0	.500
	3		2	0	1513.	752.	1.0	2.0	1085.	806.	1.0	1.0	.500
	4		1	0	3358.	491.	1.0	2.0	1548.	521.	1.0	4.0	.500
	4		2	0	1513.	752.	1.0	2.0	1486.	794.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

40' Boat	11	14 0900 Nov 72	14 1000 Nov 72	J T Welch
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
1 2 3 4 5 6	7 8 9 10	11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	31	32 33 34 35	36 37 38 39 40	41 42 43 44 45	46 47 48 49 50	51 52 53 54 55	56 57 58 59 60	61 62 63 64 65	66 67 68 69 70	71 72 73 74 75	76 77 78 79 80
1,1,1,472	5	HOPKINS MARINE STA	1	0	1786.	484.	1.0	2.0	606.	651.	1.00	8.0	.5PP
	5		2	0	1129.	730.	1.0	2.0	2638.	1859.	1.00	1.00	.500
	6		1	0	1786.	484.	1.0	2.0	1409.	519.	1.00	4.0	.500
	6		2	0	1120.	730.	1.0	2.0	1583.	714.	1.00	1.0	.505
	7	DEL MONTE BEACH	1	0	1242.	456.	1.0	2.0	1514.	494.	1.00	4.0	.502
	7		2	0	1139.	716.	1.0	2.0	1549.	762.	1.00	1.00	.50[illegible]
	8		1	0	1242.	456	1.0	2.0	1783.	505.	1.00	4.0	.500
	8		2	0	1130.	746.	1.0	2.0	1723.	749.	1.00	1.00	.500

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U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

110' Kaimt	12	160800 Nov 72	161400 Nov 72	Frederick
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
11/16/72	1	DEL MONTE BEACH	1	0	1902.	456.	1.0	2.0	1409.	461.	1.0	4.0	.500
	1		2	0	1295.	677.	1.0	2.0	1711.	674.	1.0	1.0	.500
	2		1	0	1907.	431.	1.0	2.0	1291.	470.	1.0	4.0	.500
	2		2	0	1295.	677.	1.0	2.0	1711.	671.	1.0	1.0	.500
	20		1	0	1969.	450.	1.0	2.0	1296.	484.	1.0	8.0	.500
	20		2	0	1346.	682.	1.0	2.0	1149.	718.	1.0	2.0	.500
	11		1	0	1969.	450.	1.0	2.0	2082.	469.	1.0	8.0	.500
	11		2	0	1346.	682.	1.0	2.0	1978.	715.	1.0	2.0	.500
	3		1	0	1783.	456.	1.0	2.0			1.0	4.0	.500
	3		2	0	1182.	718.	1.0	2.0			1.0	1.0	.500
	4		1	0	1383.	446.	1.0	2.0	1509.	516.	1.0	4.0	.500
	4		2	0	1182.	718.	1.0	2.0	1919.	721.	1.0	1.0	.500
	5		1	0	1783.	446.	1.0	2.0	1851.	513.	1.0	4.0	.500
	5		2	0	1182.	718.	1.0	2.0	1885.	808.	1.0	1.0	.500
	6		1	0	1783.	446.	1.0	2.0			1.0		.500
	6		2	0	1182.	718.	1.0	2.0			1.0		.500
	7		1	0	1283.	456.	1.0	2.0	1567.	530.	1.0	4.0	.500
	7		2	0	1182.	718.	1.0	2.0	1969.	741.	1.0	1.0	.500
	8		1	0	1783.	456.	1.0	2.0	1608.	459.	1.0	4.0	.500
	8		2	0	1182.	718.	1.0	2.0	2061.	719.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

40' Bott	12	160800 NOV 72	161400 NOV 72	Stoddard
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
111672	9	DEL MONTE BEACH	1	0	1783.	464.	1.0	2.0	1813.	513.	1.0	4.0	.50P
	9		1	0	1182.	718.	1.0	2.0	489.	715.	1.0	4.0	.50P
	10		1	0	1783.	464.	1.0	2.0	1797.	500.	1.0	4.0	.50P
	10		1	0	1182.	718.	1.0	2.0	2136.	740.	1.0	1.0	.50P

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

40' BOAT	13	17 0800 NOV 72	17 1400 NOV 72	JT Mitchell
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
111772	1	HOPKINS MARINE STA		1	1825.	477.	1.1	2.1	1316.	522.	1.0	4.0	.50
	1			1	1082.	710.	1.1	2.1	1759.	734.	1.0	1.0	.50
	2			1	1743.	497.	1.1	2.1	1984.	529.	1.0	4.0	.50
	2			1	1028.	729.	1.1	2.0	1486.	764.	1.0	1.0	.50
	3			1	1709.	473.	1.1	2.0	1292.	516.	1.0	4.0	.50
	3			1	1147.	764.	1.0	2.1	1690.	774.	1.0	1.0	.50
	4			1	1709.	473.	1.0	2.1	1153.	499.	1.0	4.0	.50
	4			1	1147.	764.	1.0	2.1	1491.	738.	1.0	1.0	.50
	5			1	1709.	473.	1.0	2.0	1216.	532.	1.0	4.0	.50
	5			1	1147.	764.	1.0	2.1	1969.	729.	1.0	1.0	.50
	6			1	1709.	473.	1.1	2.0	1116.	569.	1.0	4.0	.50
	6			1	1147.	764.	1.0	2.0	640.	783.	1.0	2.0	.50

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

40' KNIT	14	210900 NOV 72	21 1100 NOV 72	J T Welch
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
11 21 72	1	POINT JOE	1	1	1950.	439.	1.0	2.0	1477.	474.	1.0	4.0	.500
	1		2	1	1281.	678.	1.0	2.0	1894.	799.	1.0	1.0	.500
	2		1	1	1950.	439.	1.0	2.0	1273.	516.	1.0	4.0	.500
	2		2	1	1281.	678.	1.0	2.0	325.	794.	1.0	4.0	.500
	3	POINT PINOS SOUTH	1	1	1950.	439.	1.0	2.0	1637.	470.	1.0	4.0	.500
	3		2	1	1281.	678.	1.0	2.0	1680.	692.	1.0	1.0	.500
	4		1	1	1950.	439.	1.0	2.0	1736.	462.	1.0	4.0	.500
	4		2	1	1281.	678.	1.0	2.0	1878.	690.	1.0	1.0	.500
	5	POINT PINOS MORN	1	1	1950.	439.	1.0	2.0	1251.	490.	1.0	4.0	.500
	5		2	1	1281.	678.	1.0	2.0	1910.	694.	1.0	1.0	.500
	6		1	1	1950.	439.	1.0	2.0	—	—	1.0	4.0	.500
	6		2	1	1281.	678.	1.0	2.0	—	—	1.0	1.0	.500
	7	HOPKINS MARINE STA	1	1	1950.	439.	1.0	2.0	1420.	498.	1.0	4.0	.500
	7		2	1	1281.	678.	1.0	2.0	1721.	687.	1.0	1.0	.500
	8		1	1	1950.	439.	1.0	2.0	1362.	481.	1.0	4.0	.500
	8		2	1	1281.	678.	1.0	2.0	1739.	707.	1.0	1.0	.500
	9	DEL MONTE BEACH	1	1			1.0	2.0			1.0		.500
	9		2	1			1.0	2.0			1.0		.500
	10		1	1			1.0	2.0			1.0		.500
	10		2	1			1.0	2.0			1.0		.500

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U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST
[illegible]	15	28 0900 Nov 72	28 11-1600 Nov 72	Stancell

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
11 28 72	1	POINT JOE	1	1	18.69.	455.	1.0	2.0	2605.	493.	1.0	4.0	5.9
	1		2	1	1232.	677.	1.0	2.0	627.	724.	1.0	4.0	5.00
	2		1	1	1860.	455.	1.0	2.0	2546.	476.	1.0	4.0	5.90
	2		2	1	1232.	677.	1.0	2.0	2196.	718.	1.0	1.0	5.0
	3	POINT PINOS SOUTH	1	1	1860.	455.	1.0	2.0	2549.	472.	1.0	4.0	5.00
	3		2	1	1232.	677.	1.0	2.0	542.	697.	1.0	4.0	5.9
	4		1	1	1922.	440.	1.0	2.0	3309.	483.	1.0	4.0	5.0
	4		2	1	1265.	684.	1.0	2.0	2144.	710.	1.0	1.0	5.90
	5	POINT PINOS NORTH	1	1	1922.	440.	1.0	2.0	1729.	488.	1.0	4.0	5.05
	5		2	1	1265	684.	1.0	2.0	2662.	709.	1.0	1.0	5.0
	6		1	1	1922.	440.	1.0	2.0	1684.	462.	1.0	4.0	5.0
	6		2	1	1265.	684.	1.0	2.0	2569.	695.	1.0	1.0	5.00
	7	HOPKINS MARINE STA	1	1	1922.	440.	1.0	2.0	1950.	479.	1.0	4.0	5.0
	7		2	1	1265.	684.	1.0	2.0	1800.	721.	1.0	1.0	5.02
	8		1	1	1837.	450.	1.0	2.0	2166.	472.	1.0	4.0	5.02
	8		2	1	1235.	680.	1.0	2.0	1810.	716.	1.0	1.0	5.90
	9	DEL MONTE BEACH	1	1	1837.	450.	1.0	2.0	1932.	472.	1.0	4.0	5.00
	9		2	1	1235.	680.	1.0	2.0	3786.	689.	1.0	1.0	5.00
	10		1	1	1837.	450.	1.0	2.0	1821.	458.	1.0	4.0	5.0
	10		2	1	1235.	680.	1.0	2.0	1039.	678.	1.0	1.0	5.0

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET .

40' BOAT	16	01 0900 Dec 72	01 1400 Dec 72	J.T. Welch
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
120172	1	DEL MONTE REACH	1	1	1841.	467.	1.0	2.0	2446.	526.	1.0	4.0	.500
	1		2	1	1274.	681.	1.0	2.0	9558.	1796.	1.0	4.0	.500
	2		1	1	1841.	467.	1.0	2.0	2892.	495.	1.0	4.0	.500
	2		2	1	1274.	681.	1.0	2.0	1626.	780.	1.0	1.0	.500
	3	DEL MONTE (QUARTER)	1	1	1841.	467.	1.0	2.0	2889.	478.	1.0	4.0	.500
	3		2	1	1274.	681.	1.0	2.0	1757.	723.	1.0	1.0	.500
	4		1	1	1758.	464.	1.0	2.0	2723.	491.	1.0	4.0	.500
	4		2	1	1178.	694.	1.0	2.0	1749.	710.	1.0	1.0	.500
	5	DEL MONTE-CALCOFI 1	1	1	1758.	464.	1.0	2.0	4495.	522.	1.0	4.0	.500
	5		2	1	1178.	694.	1.0	2.0	2059.	743.	1.0	1.0	.500
	6		1	1	1758.	464.	1.0	2.0	2619.	491.	1.0	4.0	.500
	6		2	1	1178.	694.	1.0	2.0	2133.	749.	1.0	1.0	.500
	7	CALCOFI 1 (QUARTER)	1	1	1758.	464.	1.0	2.0	2988.	482.	1.0	4.0	.500
	7		2	1	1178.	694.	1.0	2.0	2065.	708.	1.0	1.0	.500
	8		1	1	1808.	454.	1.0	2.0	3035.	491.	1.0	4.0	.500
	8		2	1	1204.	683.	1.0	2.0	1984.	741.	1.0	1.0	.500
	9	CALCOFI 1	1	1	1808.	454.	1.0	2.0	3242.	476.	1.0	4.0	.500
	9		2	1	1204.	683.	1.0	2.0	2249.	728.	1.0	1.0	.500
	10		1	1	1808.	454.	1.0	2.0	3250.	470.	1.0	4.0	.500
	10		2	1	1204.	683.	1.0	2.0	2214.	730.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

40' Boat	18	07 0830 Dec 72	07 1400 Dec 72	J T Welch
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
120772	1	DEL MONTE BEACH	1	0	1906.	445.	1.0	2.0	2209.	503.	1.0	4.0	.500
	1		2	0	1219.	690.	1.0	2.0	2363.	705.	1.0	1.0	.500
	2		1	0	1906.	445.	1.0	2.0	2179.	491.	1.0	4.0	.500
	2		2	0	1219.	690.	1.0	2.0	566.	703.	1.0	4.0	.500
	3		1	1	1804.	480.	1.0	2.0	2641.	484.	1.0	4.0	.500
	3		2	1	1086.	678.	1.0	2.0	1806.	710.	1.0	1.0	.500
	4		1	1	1804.	480.	1.0	2.0	2297.	500.	1.0	4.0	.500
	4		2	1	1086.	678.	1.0	2.0	1450.	765.	1.0	1.0	.500
	5		1	3	1703.	466.	1.0	2.0	2658.	508.	1.0	4.0	.500
	5		2	3	1150.	697.	1.0	2.0	1561.	852.	1.0	1.0	.500
	6		1	3	1703.	466.	1.0	2.0	2670.	512.	1.0	4.0	.500
	6		2	3	1150.	697.	1.0	2.0	2318.	735.	1.0	1.0	.500

U. S. NAVAL POSTGRADUATE SCHOOL
DEPARTMENT OF OCEANOGRAPHY

DISSOLVED GASES DATA SHEET

110' Knorr	70	1-0330 Dec 72	14 1200 Dec 72	Fredericks
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
1 2 3 4 5 6	7 8 9 10	11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	31	32 33 34 35	36 37 38 39 40	41 42 43 44 45	46 47 48 49 50	51 52 53 54 55	56 57 58 59 60	61 62 63 64 65	66 67 68 69 70	71 72 73 74 75	76 77 78 79 80
1,21,472	1	CALCOFI 1	1	1	9.58	4.66	1.0	2.0	2071	485	1.0	4.0	.50
	1		2	1	1321	694	1.0	2.0	1930	723	1.0	1.0	.50
	2		1	1	1955	466	1.0	2.0	2267	484	1.0	4.0	.50
	2		2	1	1321	694	1.0	2.0	2181	723	1.0	1.0	.56
	3	CALCOFI 1 (QUARTER)	1	1	1959	450	1.0	3.0	2174	482	1.0	4.0	.55
	3		2	1	1346	682	1.0	2.0	1719	735	1.0	1.0	.55
	4		1	1	1959	450	1.0	2.0	—	—	1.0	4.0	.55
	4		2	1	1346	682	1.0	2.0	—	—	1.0	1.0	.56
	5	CALCOFI UNDER MONTE	1	1	1996	467	1.0	2.0	2049	473	1.0	4.0	.50
	5		2	1	1368	680	1.0	2.0	1523	725	1.0	1.0	.50
	6		1	1	1996	467	1.0	2.0	2124	487	1.0	4.0	.50
	6		2	1	1368	680	1.0	2.0	1526	709	1.0	1.0	.50
	7	DEL MONTE (QUARTER)	1	1	1949	454	1.0	2.0	2858	485	1.0	4.0	.50
	7		2	1	1337	679	1.0	2.0	1877	754	1.0	1.0	.50
	8		1	1	1949	454	1.0	2.0	2018	479	1.0	4.0	.50
	8		2	1	1337	679	1.0	2.0	1957	746	1.0	1.0	.50
	9	DEL MONTE BEACH	1	1	1986	466	1.0	2.0	3554	494	1.0	4.0	.50
	9		2	1	1355	698	1.0	2.0	1886	738	1.0	1.0	.50
	10		1	1	1986	466	1.0	2.0	3529	499	1.0	4.0	.55
	10		2	1	1355	698	1.0	2.0	1884	744	1.0	1.0	.50

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DISSOLVED GASES DATA SHEET

40' BOAT	21	15 0500 Dec 72	15 1900 Dec 72	J.T. Wetlaufer
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
121572	1	POINT JOE	1	1	3521.	454.	1.0	1.0	2321.	502.	1.0	4.0	.500
	1		2	1	3419.	695.	1.0	1.0	3526.	797.	1.0	1.0	.500
	14		1	1	3531.	454.	1.0	1.0	2162.	537.	1.0	4.0	.500
	14		2	1	3419.	695.	1.0	1.0	3009.	750.	1.0	1.0	.500
	15	POINT PINOS SOUTH	1	1	2016.	464.	1.0	2.0	2199.	579.	1.0	4.0	.500
	15		2	1	1285.	668.	1.0	2.0	2016.	799.	1.0	1.0	.500
	16		1	1	2016.	464.	1.0	2.0	2407.	493.	1.0	4.0	.500
	16		2	1	1285.	668.	1.0	2.0	3006.	722.	1.0	1.0	.500
	17	POINT PINOS NORTH	1	1	2021.	461.	1.0	2.0	2191.	494.	1.0	4.0	.500
	17		2	1	1363.	703.	1.0	2.0	3440.	718.	1.0	1.0	.500
	18		1	1	2021.	461.	1.0	2.0	2081.	475.	1.0	4.0	.500
	18		2	1	1363.	703.	1.0	2.0	3220.	707.	1.0	1.0	.500
	19	HOPKINS MARINE STA	1	1	2039.	467.	1.0	2.0	2189.	482.	1.0	4.0	.500
	19		2	1	1348.	719.	1.0	2.0	2258.	750.	1.0	1.0	.500
	20		1	1	2039.	467.	1.0	2.0	2096.	498.	1.0	4.0	.500
	20		2	1	1348.	719.	1.0	2.0	3491.	714.	1.0	1.0	.500
	21	HOPKINS-CALCOFI L	1	1	1997.	465.	1.0	2.0	2131.	479.	1.0	4.0	.500
	21		2	1	1361.	706.	1.0	2.0	1886.	695.	1.0	1.0	.500
	22		1	1	1997.	465.	1.0	2.0	2131.	486.	1.0	4.0	.500
	22		2	1	1361.	706.	1.0	2.0	1882.	735.	1.0	1.0	.500

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DISSOLVED GASES DATA SHEET

40' Boat	21	15 0900 Dec 72	15 1300 Dec 72	J.T. Wilcox
VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
12/15/72	24	CALCOFI 1	1	1	1992.	465.	1.0	2.0	3191.	487.	1.0	4.0	.520
"	24	"	2	1	1361.	706.	1.0	2.0	1727.	729.	1.0	1.0	.500

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DISSOLVED GASES DATA SHEET

VESSEL	CRUISE NO.	DATE/TIME COLLECTED	DATE/TIME ANALYZED	ANALYST

DATE	BOTT. NO.	LOCATION	COMP	DEPTH (M)	H CAL	W CAL	RANGE CAL	ATTEN CAL	H COMP	W COMP	RANGE COMP	ATTEN COMP	VOLUME (L)
					1361.	5112.							
					903.	741.							
					1360.	514.							
					940.	716.							
					1325.	514.							
					883.	713.							
					1283.	508.							
					903.	720.							
					1365.	526.							
					920.	769.							
					1330.	507.							
					912.	762.							
					1324.	515.							
					899.	758.							
					1295.	505.							
					894.	784.							
					1250.	506.							
					828.	730.							
					1230.	515.							
					840.	739.							

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ABSTRACT

A system for the determination of dissolved gases in seawater by gas chromatography was constructed and used to find the concentrations of methane and carbon monoxide in a variety of habitats around the Monterey Peninsula. Methane was shown to have a maximum of 2.8×10^{-4} ml/l at 50 meters at the open ocean station, with a surface value of 1.1×10^{-4} ml/l. The surface waters at the nearshore stations were almost three times this value. Methane was also shown to be an effective tracer for sewage effluent. The carbon monoxide maximum of 2.1×10^{-4} ml/l was found at 15 meters which correlated closely with primary productivity (Rowney 1973). The surface values of 0.81×10^{-4} ml/l was lower than the nearshore values. All stations sampled were found to be highly supersaturated with both gases. This indicates that in this area, the ocean is a major source of both methane and carbon monoxide.

KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
gas chromatography						
methane						
carbon monoxide						
dissolved gases						
gradient analysis						
gas analysis						
seawater analysis						
pollution